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A review on electronic spectroscopy of perylene

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A REVIEW ON

ELECTRONIC SPECTROSCOPY OF PERYLENE

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by

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A REVIEW ON
ELECTRONIC SPECTROSCOPY OF PERYLENE

by Surjit Kaur

Literature research of Polycyclic Aromatic Hydrocarbons reveals that luminescence of these molecules at low temperature is of astrophysical interest. This class of compounds is postulated as one of the major repository of interstellar carbon. Absorption, Fluorescence and Electron-ion recombination are some of the probable processes that occur under physical conditions of the Interstellar Medium.

This thesis is a review of spectroscopic studies on perylene that provides an overview of spectral features of this molecule. Absorption and fluorescence features of neutral and cationic perylene are discussed. Latest results and technique of electron-ion recombination process in perylene are also discussed and analyzed. These results are based on the laboratory observations of experiments performed by Allamandola and Co-workers.

Acknowledgments

The final product of a research is not an individual effort. It takes suggestions and assistance of several others. I owe acknowledgments to many people who have influenced my research work in different ways.

I am indebted to Dr. Lou Allamandola of Astrochemistry group of NASA Ames Research Center for allowing me to do this research work at the facility. I am especially grateful to Dr. Xavier Chillier for allowing me to observe experimental details and helping me better understand the insights of technique of Matrix-Isolation.

My sincere gratitude goes to Dr. Brad Stone, my research advisor, for assigning me this interesting project. This thesis is a result of his continual advising and interest in the subject.

Special thanks to my family for tolerating my absence at get-togethers. For giving me all the support and encouragement.

Lastly, I would like to dedicate this thesis to the memory of the person who inspired me to continue on with education. My best friend, philosopher and guide- S. Baldev Singh -My father.

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CHAPTER I: INTRODUCTION

A. GENERAL:

This thesis presents a review of absorption and fluorescence features of perylene. Perylene is a non-aromatic molecule that belongs to the class of organic compounds known as Polycyclic Aromatic Hydrocarbons or PAHs.

Luminescence features of perylene discussed here are mainly those that were observed with matrix-isolation spectroscopy, and Shpol'skii matrices. Results from other techniques are also briefly discussed.

A detailed discussion on electron-ion recombination process of perylene cation in argon matrix is presented. This discussion is based on on-site observation and analysis of experiments performed by Chillier et. al.[1] at the Astrochemistry lab of NASA Ames Research Center in Moffet Field, CA.

Selection of perylene as the molecule of interest follows from the astronomical interest of the Astrochemistry group at NASA Ames.

A brief summary of some astronomical conditions and a brief background to assignment of PAHs as a constituent of the interstellar matter is given in the following sections:

B. INTERSTELLAR MEDIUM :

The Interstellar Medium (ISM) is a broad term that refers to the matter and gases existing between stars. The ISM is made up of clouds of gas that are mainly composed of atoms, molecules and ions of hydrogen. In this gaseous atmosphere, smaller ratios of heavy elements and other molecules have also been detected [2].

Earlier in the 20th century, it was established that the interstellar medium contains a significant amount of microscopic solid particles that are composed of carbon and silicates coated with water ice. These particles are collectively known as 'Interstellar Dust'. The interstellar dust and gases collectively form vast clouds and these tenuous clouds are sometimes visible, or partially visible in the form of nebulae (Latin for Clouds).

Absorption of light by these clouds creates large dark regions in the galaxies. The nebulae are more often invisible to ordinary light. The interstellar medium is detectable due to the absorption and emission of radiation by nearby stars, or simply by the scattering of radiation. The classification of interstellar matter is deduced from observation in the ultraviolet, infrared, x-ray, and radio regions of the spectrum.

Interstellar matter is not uniformly spread throughout the galaxy but is clumped together in the interstellar clouds that vary in size and complexity. The stars of The Milky Way, and presumably, stars in all the billions of Galaxies in the Universe are born in interstellar clouds. When they come to the end of their lives, many start to throw off matter that mixes with the interstellar medium. This results in the formation of new interstellar clouds that eventually forms a star. In summary, stars form from the interstellar matter and throughout their lives, they structure and transform the interstellar medium.

Interstellar space is emptier than best vacuums that can be produced artificially in an Earth-based laboratory. The ISM makes up about 10% to 15% of the visible mass of

Milky Way. One observation that can be drawn is that there must be very little amount of matter present in the ISM, otherwise it would absorb all of the starlight.

About 99% of ISM is gas and the remaining 1% is interstellar dust having density as low as 10^{-4} molecules per cubic cm. The dust is composed of carbon, metals, silicates and ice. Dust grains are approximately 1-3000nm in size, and have a density of approximately 1 per million cubic meter. Graphite has a very minimal possibility of existing in the interstellar medium [2].

The ISM shows large variation in temperature as well as structure. Some regions consist of dense clouds with temperature below 10 °K, while others consist of lower density regions at temperatures of million degrees Kelvin. The interstellar medium is dynamic. There is an ongoing activity of cloud formation, collisions, coalescence, and fragmentation to form new stars.

Stars produce cosmic rays and magnetic fields due to the processes that occur in their interiors. As cosmic rays pass through this medium, along with the effects of magnetic fields, the interstellar medium yields new components which are important to study as well.

It has been established that the dust is not an isolated phase of the ISM. It exists as a mixture of cold and hot gases in the Photodissociation Region (PDR). It may exist in neutral or ionized forms. The ionization theory for the stellar atmospheres was originally applied by the physicist M. N. Saha. An ionization equation was established to evaluate the percentages of ionic species versus the neutral molecules present in the ISM [3]. For a

long time, this theory dealt with the metals and smaller atoms [4]. Similar approximations are now being applied to investigate the presence of any larger molecules in the interstellar atmospheres.

Understanding the make up of ISM helps in better understanding of the origin and evolution of planetary atmospheres in the universe. These studies on ISM also shed light on several processes that occur in the ISM due to interactions with other species, or with highly energetic, or charged particles.

C. BIRTH OF STARS IN MOLECULAR CLOUDS:

Star formation is the process during which the generally rarefied components of the ISM condense into a dense physical state i.e., a star. So far, the process of star formation is not completely understood. Most likely, some of the gas and dust is somehow compressed locally into a mass that can no longer resist its own gravity. This mass collapses in a runaway manner and eventually turns into a star.

Astronomical observations by various scientists suggested that most star formations take place in the interiors of giant, dark, dense and cold conglomerates called molecular clouds. Molecular clouds are the dense regions of ISM. One of the vastly studied star nurseries is the Orion region. Large molecular clouds can be seen in the middle of the dagger of Orion. The Trapezium cluster of Orion is made up of very luminous stars. These stars are approximately 2 million years old [5].

The dense interiors of the molecular clouds cannot be observed with visible light. The dust in these molecular clouds shields the interstellar interior from visible radiation.

Using the new techniques of infrared and millimeter radio astronomy, it is possible to measure the conditions inside these clouds and to study the early stages of star-birth.

When a star is formed, it emits copious amounts of ultraviolet radiation and surrounding gases in the molecular cloud heat up due to exposure to radiation. The radiation causes expansion in the gases. Supernova explosions may also cause the gas to expand. The hot gases explode into the surrounding cold cloud, which compresses the material in it until the cold gas is at the same pressure as expanding hot gas. In the conditions typical of molecular clouds, this compression is enough to increase the gas density by a factor of 100. At these densities, star formation occurs in the interior of compressed gas [6].

Star formation creates carbon in the interior of a star core and releases it into space, making carbon an ideal probe and tracer of the birth and death of stars, planetary systems, and of the processes in deep interstellar space. As a result of these supernovae explosions, organic molecules may form, but only molecules that are capable of tolerating the harsh conditions of interstellar medium can survive.

D. ABSORPTION BY MOLECULAR CLOUDS :

The detection of molecules in the interstellar medium is considerably important from the astronomical point of view. Existence of interstellar matter was postulated due to the dimming of starlight by the material between the stars and point of observation. The absorption spectrum of the interstellar medium is studied based on the emission spectra of the star behind the interstellar dust.

Due to the presence of molecules and the temperature and pressure conditions, the characteristic absorption by the interstellar medium is always greater at shorter wavelengths. As a result of this absorption, the blue light from the stars is dimmed as it passes through the interstellar medium. Therefore, stars appear redder than they would if there was no interstellar medium present.

The variation of absorption intensity with distance and direction provides information about the contribution and the extent of absorption by the interstellar medium. One example of different degrees of absorption of starlight is the Orion Nebula. The molecular clouds in this nebula absorb sunlight that originates from the stars located in the core of Orion. Features of various intensities can be seen depending upon the thickness of the interstellar medium.

From the study of absorption and emission spectra of the ISM, chemical composition of molecular clouds may be deduced. Presence of molecules is most dense where the stars appear to be forming and in the outer atmosphere of the cool stars.

One big discovery towards identification of molecules in the ISM occurred in 1963 when OH^- ion was detected due to absorption studies by Radio Astronomers. Later, in 1967, water was identified in the microwave emission at 1.35 cm [7]. Soon after that, ammonia was detected, and since then, the database of molecules detected in interstellar space has significantly increased. Studies on the physical conditions of the interstellar medium have established that the physical conditions of the molecules are quite different from those on Earth. Hence it is important to study these molecules at physical conditions that mimic the interstellar conditions.

E. ASTRONOMICAL IMPLICATIONS OF LUMINESCENCE PROCESSES:

In interstellar clouds of low to moderate density, there is substantial abundance of various types of molecules. Several theories have been established to speculate the formation of these molecules. Various theories have been proposed that include: 1) Formation of molecules on the surface of dust particles that exist in the interstellar medium, 2) Collision of atoms with one another and formation of new species, and 3) formation of new molecules from the evaporation and decomposition of dust particles when they encounter heating phenomenon such as energetic particles or photons [7], and 4) energetic supernovae explosions.

The species once formed in the ISM lead to several types of interactions of molecules with one another. There are approximately 40 types of interactions that these molecules can undergo, e.g. Photodissociation, Electron-Ion recombination, Charge Exchange, Chemical Exchange, etc.[8]

In low temperature molecular clouds, mobilities of the species are low. Ultraviolet radiation from the starlight can cause these molecules to exist in neutral, cationic, and anionic states.

The principle of electron-ion recombination states that if a previously ionized molecule comes in contact with an electron, it will bind to it and produce neutral species. This process may be visible spectroscopically depending upon the temperature of the medium and the type of molecules present. This process will also depend upon the distance from a star that would provide enough UV radiation to photolyze these species.

The presence and identification of molecules in the ISM can be established by performing Earth-based luminescence studies on the molecules that are expected to be present in the ISM. The spectral features of an Earth-based experiment can be compared to those taken by the space telescopes. The comparison of these features is based on the regions of emission rather than individual spectral features. Interstellar spectra is a combination of several molecular species present in the ISM. Various molecules may be present in different ratios in the different regions. Luminescence studies give a general overview of the type of molecules that may be present in the ISM, as deduced from the spectral properties.

F. PAH HYPOTHESIS:

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of compounds made up of only carbon and hydrogen and have more than one aromatic ring in their structure. On Earth, they are best known as cancer-causing air pollutants created by partial combustion such as: sooting flame, diesel exhaust, charred hamburgers, and cigarette smoke. PAHs may be created naturally in forest fires, and in volcanic eruptions. In the interstellar space, PAHs are believed to be formed as a result of supernovae explosions.

In the interstellar space, some species may be more abundant than others depending on their stability against the interstellar UV radiation field. Beyond the Earth, towards the interstellar medium, PAHs have been postulated as an important component of the interstellar medium. PAH model for ISM was introduced by Leger and Puget in 1984 and Allamandola et. al. in 1985. This deduction comes from the high stability of PAHs against ultraviolet radiation and the harsh physical conditions of the interstellar

space. This is also deduced from the close resemblance of their infrared spectral features with the IR emission bands of the ISM observed between 3.2 and 14.0 μm.

In 1989, Allamandola et. al. hypothesized the ionized PAH model for interstellar matter [9]. This model postulates the presence of PAHs in interstellar medium as a mixture of free, neutral and ionized gas phase molecules.

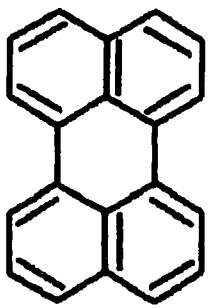
The term PAH has extended from small molecules (< 20 carbon atoms) to large graphitic platelets. Such a definition, however, is unnecessarily restrictive as it would pertain to purely aromatic compounds containing only carbon and hydrogen. Therefore the term PAH has now been taken over by more descriptive term of Polycyclic Aromatic Compounds [10]. This broader term now includes: (1) polycyclic aromatic compounds that incorporate heteroatoms such as nitrogen or oxygen in their structure, (2) polycyclic aromatic rings that carry functional groups or aliphatic sidechains, hexabenzocoronene has been the largest compound studied from this category, (3) polycyclic aromatic compounds that are partially hydrogenated or superhydrogenated e.g. H_n-PAHs, and (4) aromatic compounds with some non-aromatic character e.g. perylene.

Structures of some of the PAHs can be seen in figure A. Some or all of these compounds are legitimate candidates for the spectral features observed within the interstellar medium. All of the compounds that fall in the above categories are referred to as PAHs.

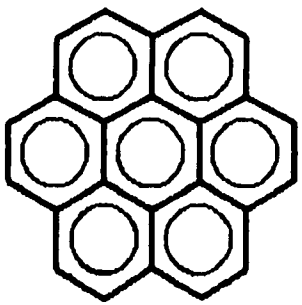
PAHs are considered to be plausible candidates for the diffuse interstellar bands (DIBs) [11,12]. DIBs are visible absorption features observed in the spectrum of interstellar matter. It has been quite recently recognized that their carriers can relax radiatively.

The ISM environment produces a mixture of neutral as well as positively and negatively charged PAHs. The amount of each depends upon the physical conditions of the ISM. Considering PAHs as the DIBs carriers, it is important to study their physical and luminescence properties in the neutral and ionic forms [13].

PERI-CONDENSED



Perylene



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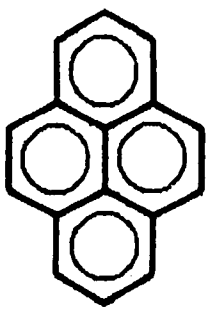
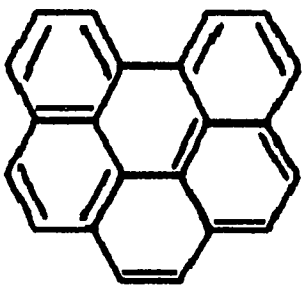
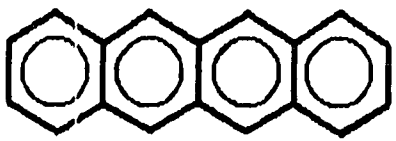


Pyrene

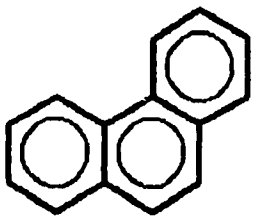


Benzo[ghi]perylene

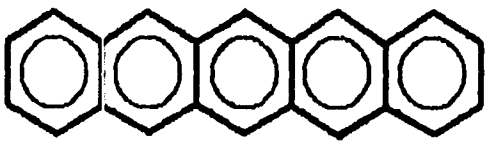
CATA-CONDENSED



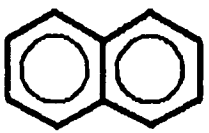
Tetracene



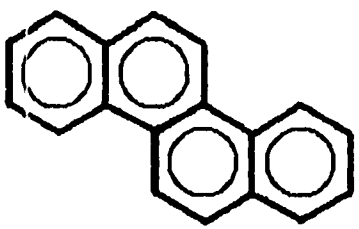
Phenanthrene



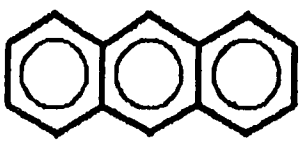
Pentacene



Naphthalene



Chrysene



Anthracene

FIGURE A : Some Simple Polycyclic Aromatic Hydrocarbons (PAHs)

CHAPTER II. SPECTROSCOPIC METHODS

PAHs exist in the gas phase in ISM. These molecules are isolated from each other and experience minimal intermolecular interactions. In Earth-based laboratories, Gas phase studies on PAHs are difficult to perform as larger PAHs (>20 carbon atoms) are highly refractory materials.

With present technology, several techniques are available to study polycyclic aromatic hydrocarbons at low temperatures. Some of those techniques are: Matrix Isolation spectroscopy, Supersonic Jet spectroscopy and Shpol'skii matrices. Only matrix isolation and Shpol'skii matrices will be discussed here in detail. Details on Jet spectroscopy experiments on perylene can be found in References 14 and 15 .

A. MATRIX- ISOLATION SPECTROSCOPY:

At the beginning of 1950s, Norman and Porter [16], and about the same time, Whittle et.al. [17], independently of one another, developed the technique of matrix isolation. It is a technique that allows one to study the species of interest suspended in a frozen inert gas matrix. It involves the use of a non-reactive gas, i.e. noble gases as the matrix. This technique allows one to freeze reactive intermediates and unstable compounds at normal conditions in a rigid matrix at about 4-40 °K. This technique has been successfully employed in several laboratories for spectroscopic studies of neutral and ionized PAHs under astrophysically relevant conditions.

The deposition times for this technique are based on the fact that interstellar dust receives occasional doses of ultraviolet light from the stars. Each hour of radiation in the lab is reckoned to mimic what the interstellar dust would receive in a thousand years.

The low temperature required is achieved by cryostats. At these temperatures and below, the matrix is considered rigid and the trapped species cannot diffuse. For Argon, temperature of 20 K or colder is required. Similarly, for Neon, 7.2 K or colder is needed. Since 10 K is the minimum temperature that most mechanical coolers can currently achieve with the reasonable cooling, argon matrices are commonly employed. In order to prepare the matrix, an excess of inert gas is condensed simultaneously with the substance of interest or a suitable precursor onto a cooled spectroscopic window, which is made of quartz or sapphire for UV, visible and near IR spectroscopy. There are very minimal interactions expected between the reaction medium and the species of interest.

During the deposition of sample on window, the molecules are spatially separated while embedded into the matrix lattice. In most cases, intermolecular reactions are ruled out at 10 °K by sufficiently high energy barriers. Reactions among species of interest are also suppressed by the high dilution of sample with noble gas.

B. SHPOL'SKII MATRICES:

Study of the luminescence features of PAHs at lower temperatures is an astrophysically relevant condition. Low temperature spectroscopy is also helpful in defining the spectral features with narrow spectral lines.

The emission spectrum of larger molecules at temperatures <100 °K, can be broad and structureless. This is due to the large number of molecular conformations in the excited state. As a result, the vibrational structure is only partially resolved.

If a solvent at a low temperature has a crystalline structure in which the solute molecule adopts a unique configuration, vibrational structure of the solute becomes more

pronounced. This phenomenon was first observed by E.V. Shpol'skii and L. A. Kilmova in late 1950's [18]. After his name, the solvent that is used for this technique is referred to as 'Shpol'skii matrix'. Some of the common Shpol'skii matrices are n-paraffins. For perylene, one of the commonly used Shpol'skii matrix is n-heptane [19]. Some of the other common matrices for perylene are: n-hexane, octane, and nonane [20].

The presence of a solvent results in a drawback of this technique. The interpretation of Shpol'skii emission spectra is complicated by multiple emission. This is due to the existence of solute molecules in different crystal environments.

B. OTHER TECHNIQUES:

Some of the other techniques that are used to study PAHs involve single molecule spectroscopy in combination with Shpol'skii matrices, [21] and Jet cooled spectroscopy [14,15].

Perylene is a suitable candidate for supersonic jet experiments. One of the features that differentiates perylene from other condensed ring compounds is the large separation between the first and second electronically excited singlet states. Due to this separation, it is possible to make detailed measurements on the absorption bands without any interfering features from other electronic states.

Fluorescence spectrum by jet spectroscopy is simplified due to depopulation of low-lying vibrational levels in the ground electronic state. This phenomenon makes jet spectroscopy far more useful than gas phase spectroscopy. [22] The vibrational structure that may sometimes be buried under the gas phase spectrum can be revealed using jet spectroscopy. The vibrational structure hence produced may be extremely useful in

obtaining information on the structure of the molecule in the ground or excited electronic state.

Jet studies produce minimal interactions between the molecules of interest. The molecules can then be studied as if they were isolated from one another. This again, is the condition of astrophysical interest.

CHAPTER III

NON-AROMATIC COMPOUND - PERYLENE :

Perylene is a five ring compound of molecular formula $C_{20}H_{12}$, with a molecular weight of 252.32. It belongs to D_{2h} molecular point group. The structure of perylene can be seen in figure B. Perylene exists as a dark brown solid in crystalline phase. In the crystalline state, perylene shows bright orange-red fluorescence. In solution, this fluorescence turns out as blue.

Perylene represents a type of condensed ring PAHs that contain formal single bonds. However, it is somewhat different from other PAHs due to structural differences. Synthesis of perylene from naphthalene [23] led chemists to consider perylene molecules as a combination of two relatively weakly bonded naphthalene nuclei.

One of the factors that make perylene distinct from other PAHs is the number of hydrogen atoms attached to it. Perylene consists of five rings in its structure, therefore according to Huckel's rule, it has 22 π electrons. This satisfies the condition for aromaticity of a molecule, and existence of electrons in the form of continuous electron clouds above and below the plane of rings.

In 1953, x-ray determinations by Donaldson et. al.[24] showed that the bond length for the two bonds that join the two naphthalene nuclei is 1.50 °A. This is shown in figure B as bond D. All the $\angle$CCC angles are at 120°. The bonds along the periphery, i.e. bonds A, B, and C, have a bond length of 1.38 °A. This bond length suggested that the two naphthalene nuclei are joined via weak single bonds. This bond is exceptionally

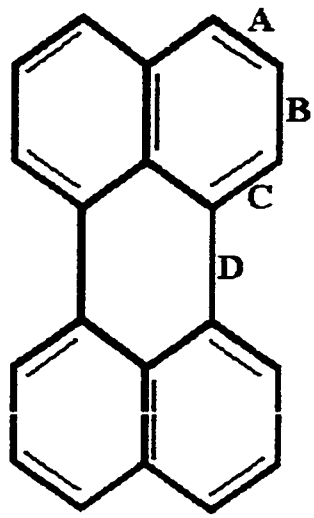


FIGURE B: Structure of Perylene molecule[24]

large according to Donaldson et. al's data. Such long bonds are not encountered in any other polycyclic aromatic hydrocarbon with sizes comparable to that of perylene.

These bond lengths were later studied by Camerman and Trotter [25] in 1963, and the resulting bond length for the bonds joining the two naphthalene nuclei was reported as 1.48 °A, which is in good agreement with Donaldson et. al's data.

Perylene has a total of 32 atoms and being a non-planar molecule, it undergoes a total of 90 vibrational transitions. Considering perylene to be made of two naphthalene molecules joined together, the vibrational transitions can be assigned as follows: 24 CC stretches, 12 CH stretches, 30 CCC bends and 24 CCH bends for the in-place vibrations, 30 CCCC torsions, and 12 CH and 4 CC out-of-plane bending for the out-of-plane vibrations [26]. These designations and assignment of the vibrational transitions are in accordance with those of naphthalene in Ref. 27 and 28.

The non-aromatic nature and absorption in visible region make perylene distinct from rest of the PAHs. As it is a member of the same family, a more appropriate classification of this molecule would be as Polycyclic Aromatic Compound.

CHAPTER IV

A. SPECTRAL FEATURES OF NEUTRAL PERYLENE

I. ABSORPTION SPECTRUM OF PERYLENE :

From the structural features, perylene can be considered to be made up of two naphthalene molecules. Perylene is a member of the extended family of PAH compounds, but the absorption characteristics of perylene significantly differentiate it from naphthalene and other PAHs. Naphthalene, as well as other PAHs having up to five to six rings, absorb in the ultraviolet region. No absorption features are seen for these molecules beyond the extreme violet region.

Perylene, on the other hand shows intense absorption in the visible region. It shows a sharp maximum at around 430 nm, for perylene isolated in an argon matrix. This feature is a resulting artifact of the totally symmetric CC stretching. Figure C shows absorption spectrum of a neutral perylene molecule[29].

The absorption spectrum of perylene represents a progression that begins around 430 nm and extends to approximately 360 nm towards the short wavelength side [20,29,30]. These features show similarity between the matrix isolated samples [Figure C] to absorption in ethyl alcohol [30] [Figure D] and normal paraffins [20,31]. In paraffins, these features shift towards the blue depending upon the solvent used. The shift for various solvent is in the order of n-hexane, heptane, octane, and nonane, with nonane exhibiting the most shift towards the shorter wavelength.

The absorption features of perylene in an argon matrix at 362, 382, 404, and 430 nm [29], have a significant match with those in solutions [20]. However there is a slight shift

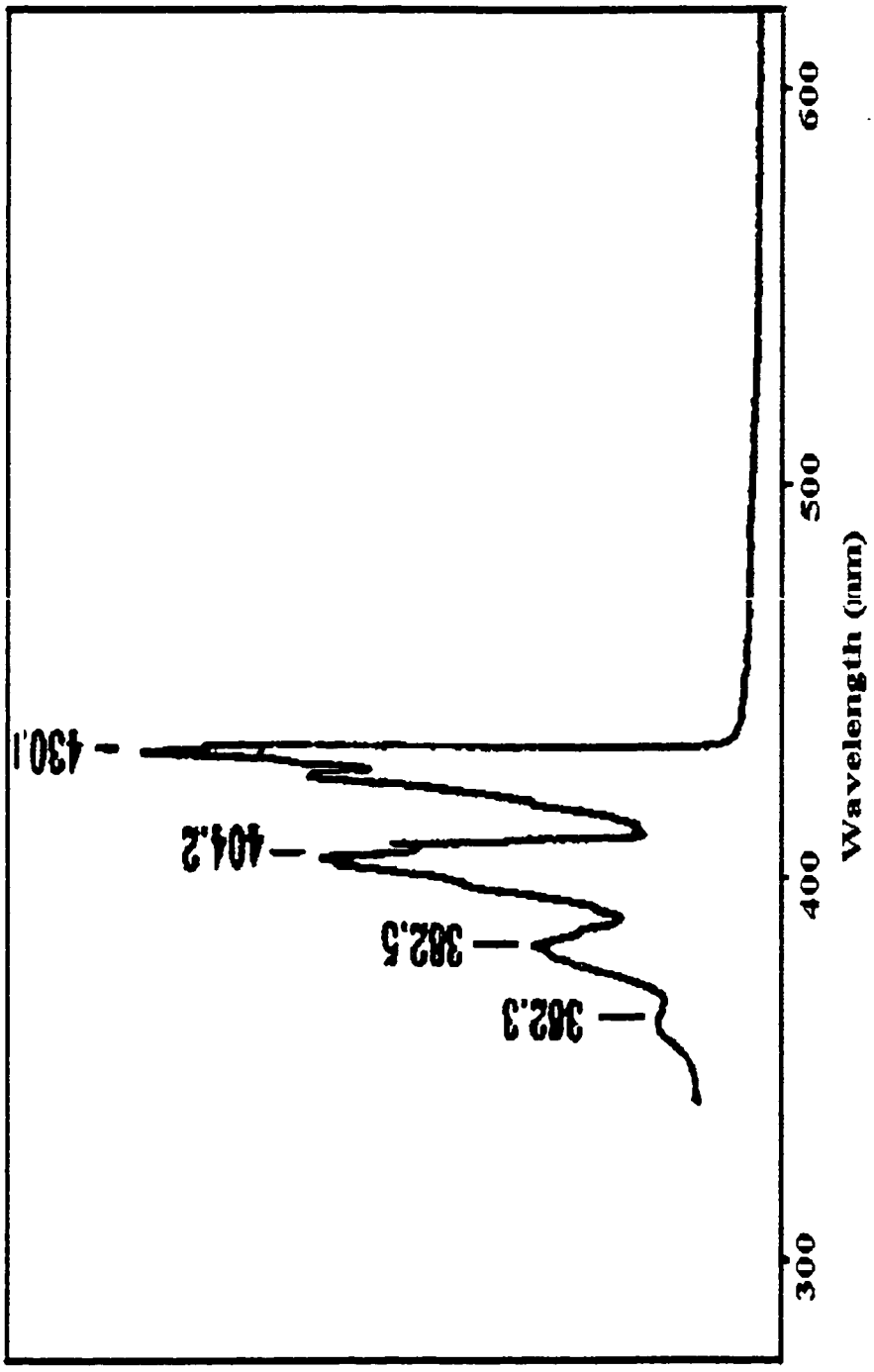


FIGURE C: Absorption features of Matrix-isolated Perylene in 300-600 nm region.[29]

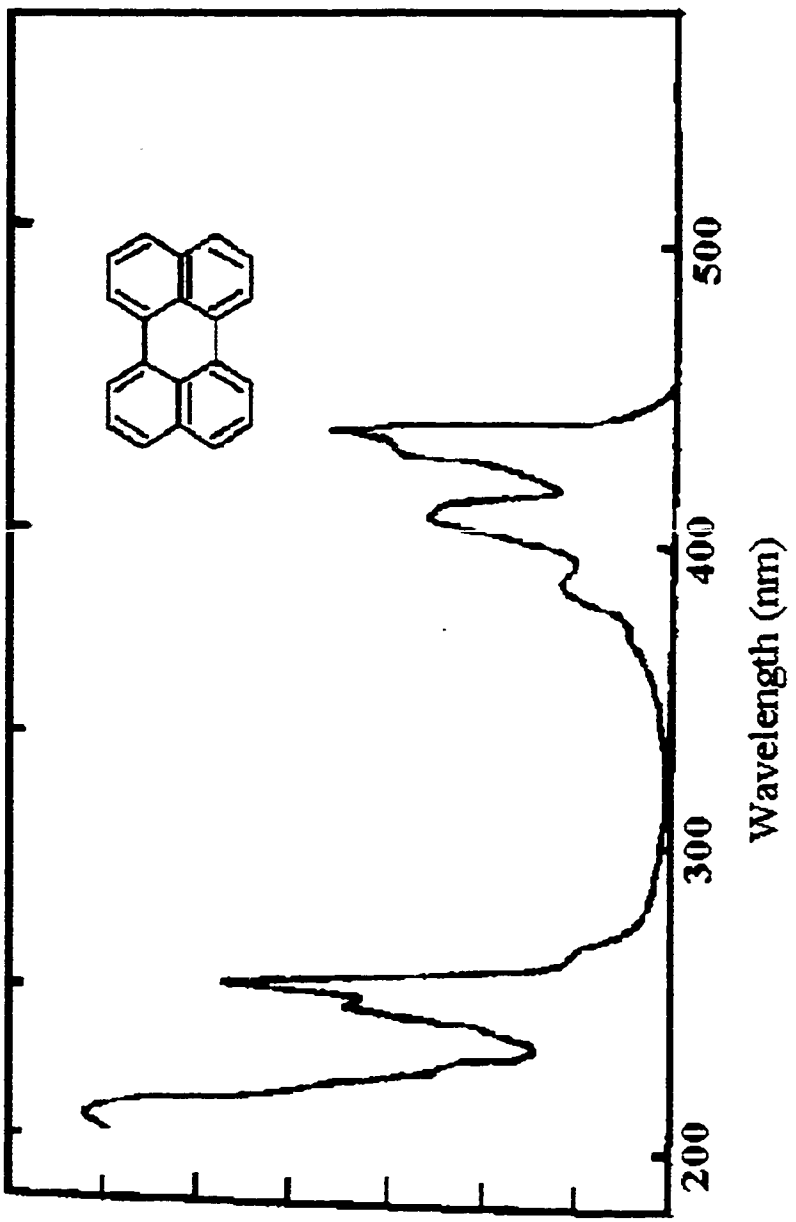


FIGURE D: Absorption spectrum of Perylene in the ethanol solution.[30]

of these features towards longer wavelength in n-hexane and ethanol at 77 K, as compared to the matrix isolated perylene in an argon matrix at 15K. The absorption spectrum of perylene can be seen in Figure E [1]. Considering that argon affects perylene molecules minimally, these features are assigned to the perylene molecule itself.

Comparing absorption features of perylene in n-hexane [20] to matrix isolated in argon [29], the absorption features in n-hexane are shifted towards higher wavelength by approximately 150 °A. A symmetric shift for the entire spectral pattern is clear from the strong features in the spectrum.

II. FLUORESCENCE OF PERYLENE :

Perylene has a bright orange red fluorescence in the crystalline state and at room temperature. The spectrum at room temperatures is diffuse and is shifted towards the longer wavelengths. A Maxima is observed around 620 nm.

In solutions, at about 77 °K, the bands are shifted towards the shorter wavelengths and the fluorescence of perylene molecule, in general, becomes blue. The bands of the fluorescence spectrum are fairly resolved at around 77 °K.

The fluorescence bands can be further resolved by lowering temperatures to 15-20 °K and using matrix isolation spectroscopy. This eliminates the interaction of perylene molecule with each other, as well as the solvent molecules. The experimental setup for matrix isolated fluorescence process can be seen in Figure F. Fluorescence spectrum of matrix isolated perylene with argon, can be seen in Figure G. The excitation

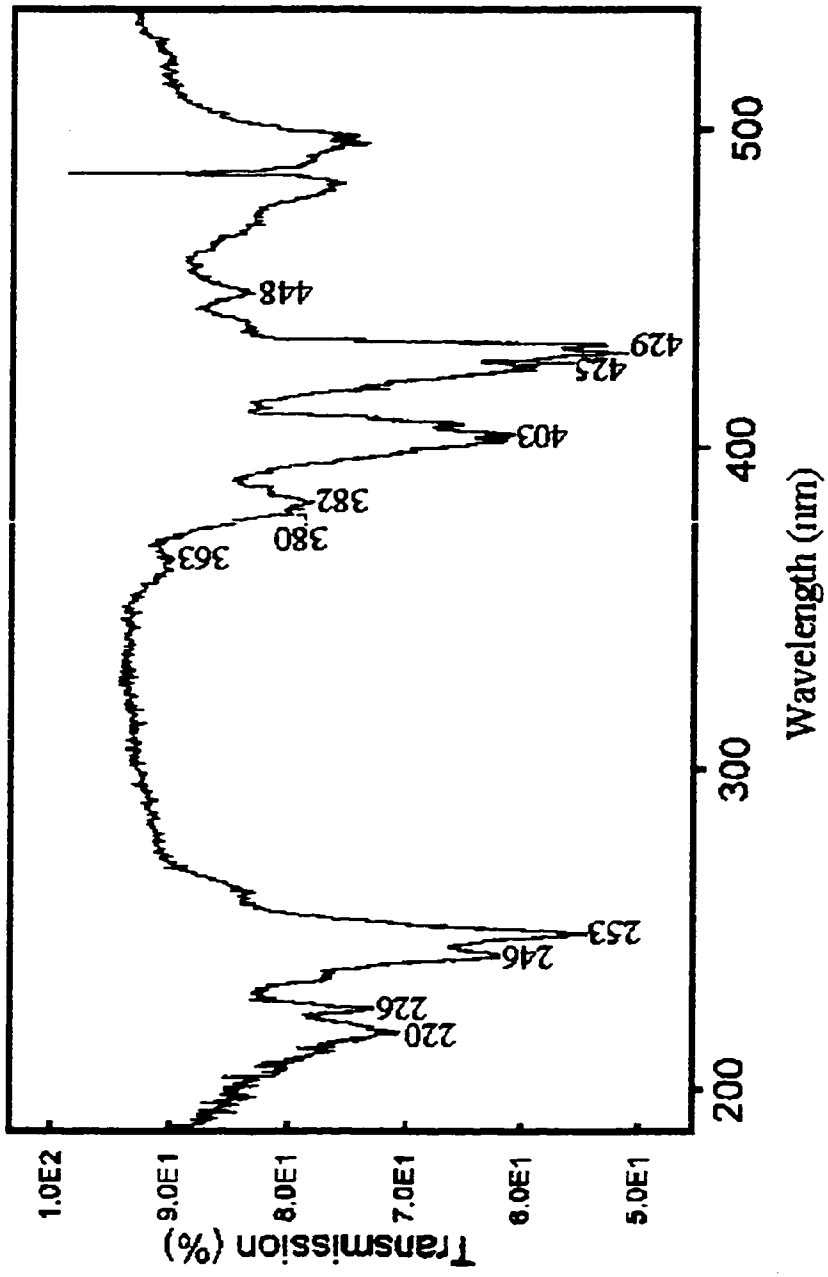


FIGURE E : Absorption spectrum of perylene in an argon matrix at 15 °K.[1]

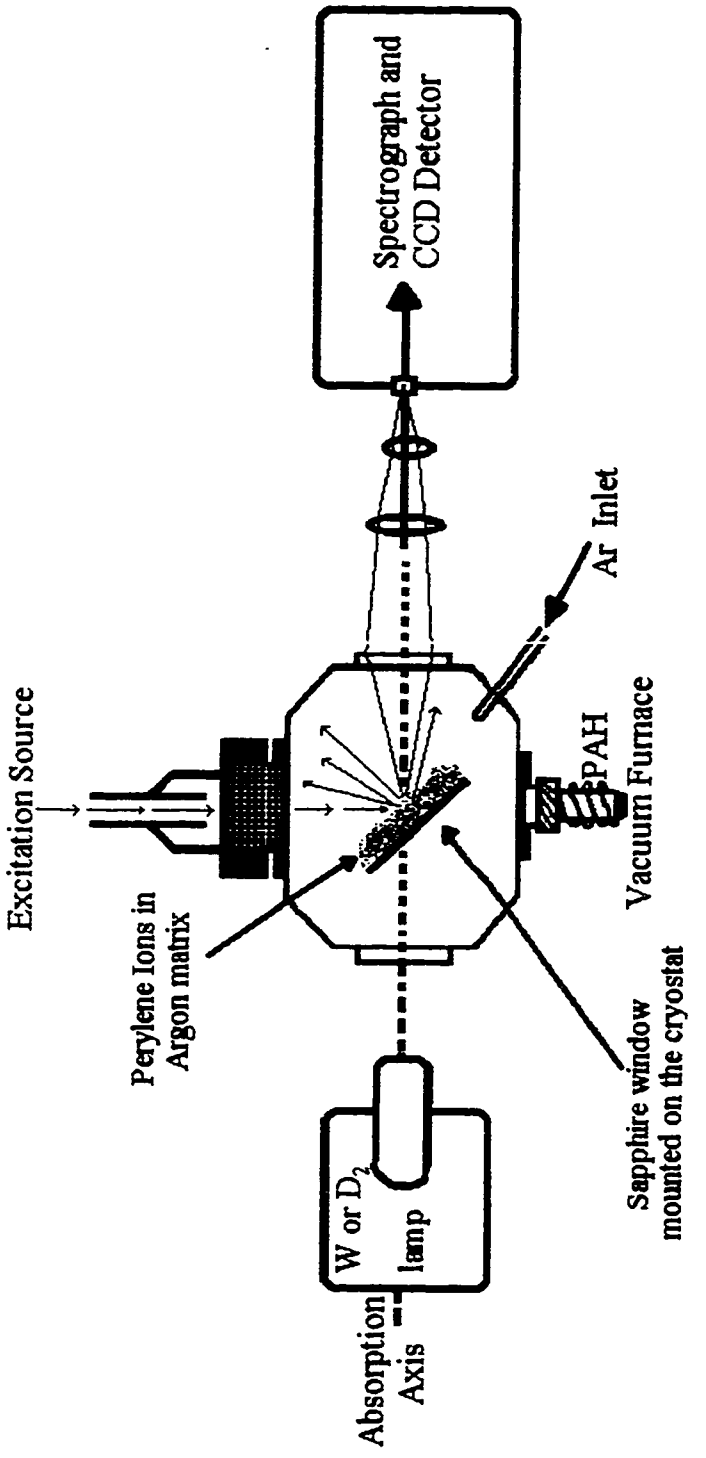


FIGURE F: Cross-sectional view of the experimental configuration for Fluorescence process.

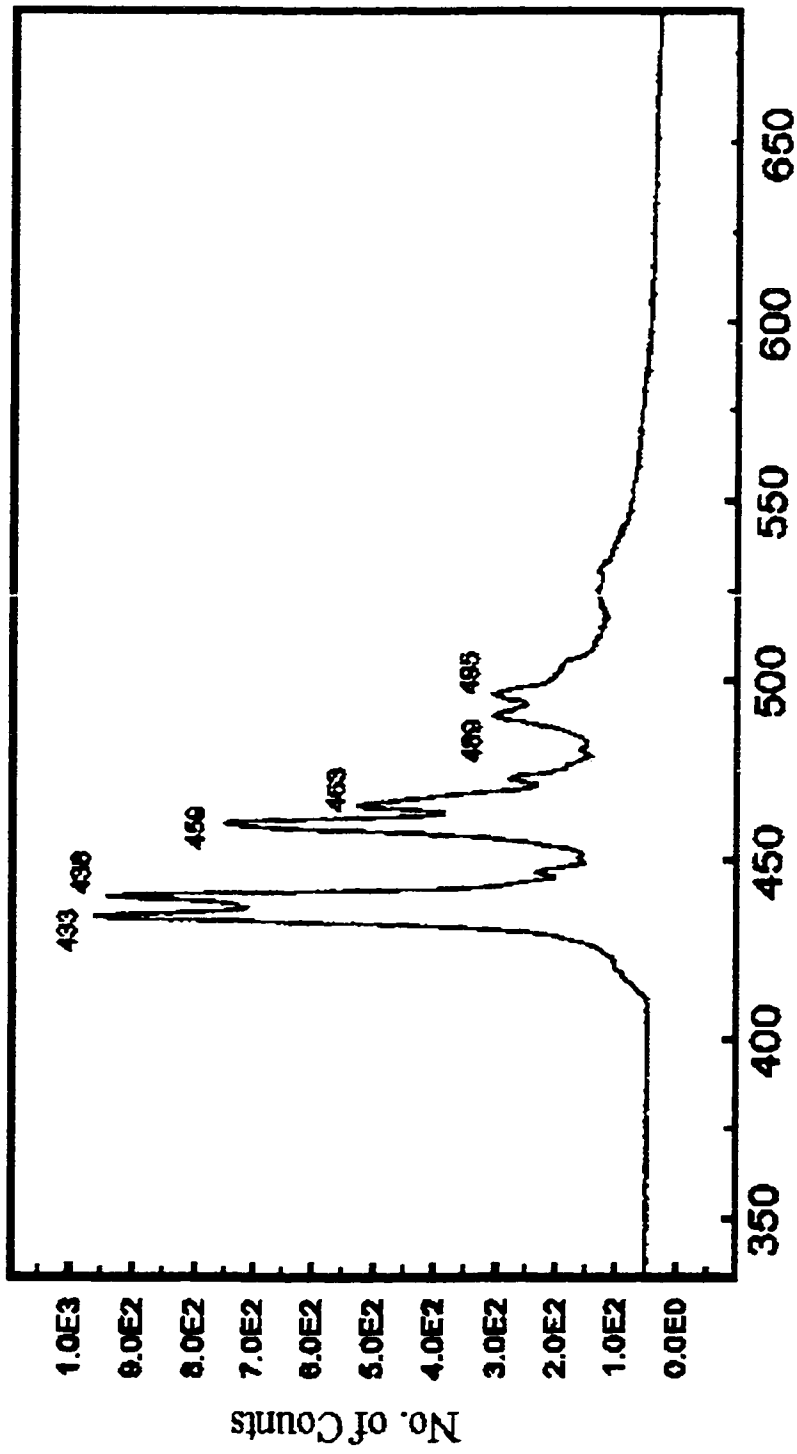


FIGURE G: Fluorescence Spectrum of Neutral Perylene in Argon matrix at 15 K.[1]

wavelength for this spectrum is set at 425 nm. The slit of the spectrograph is set to 150 μm.

Comparison of the sharp absorption and fluorescence spectra of perylene in an argon matrix at 15-20 °K, shows that the most intense short wavelength line of the fluorescence spectrum at around 430 nm, coincides with the longest wavelength intense line of the absorption spectrum. This line is, therefore, associated with the (0,0) transition.

The lines associated with absorption features of perylene can be represented as a combination and harmonics of 5 frequencies [20]. Similarly, the intervals between the fluorescence bands can also be represented by the combination of 5 frequencies. Out of these, for matrix isolated samples, the frequency combinations involving the 354 cm^{-1} and 531 cm^{-1} combinations are most intense.

Comparison of the absorption and fluorescence spectra of matrix isolated perylene appear approximately as mirror images of one another. The mirror symmetry for these features of perylene in ethyl alcohol, can be seen in Ref. 20.

Comparison of absorption features of perylene in n-hexane to matrix isolated perylene in argon indicates that fluorescence features in n-hexane are shifted towards higher wavelength by approximately 120 °A. It is a symmetric shift that is clear from the strong features of the spectrum. However, features observed beyond 540 nm in case of n-hexane are not visible for perylene isolated in an argon matrix.

B. IONIZATION OF MATRIX :

Luminescence spectra of the charged PAHs has only been reported using matrix-isolation technique. The ionization technique for matrix-isolated perylene will be discussed briefly in this section.

The absorption and fluorescence spectrum of the matrix isolated molecule define spectral features that are associated with a neutral molecule. After absorption and fluorescence experiments, the matrix can be photolyzed to perform further experiments. The same sample that is used for fluorescence and absorption processes can be used for the same purpose.

The perylene cations can be subsequently generated by *in-situ* UV photolysis of the matrix. A hydrogen discharge lamp can be mounted on a vacuum head for the photolysis. The Lyman α line (120 nm) is commonly used as the ionizing radiation. The typical experimental setup for the photolysis process can be seen in Figure H.

The photoionization of perylene in argon matrix is as follows:

$$1)\quad Per + h\nu_1 \longrightarrow Per^* \quad (S_1)$$

$$2)\quad Per^* + h\nu_2 \longrightarrow Per^+ + e^-$$

The ionization of perylene is a multi-step process. The photolysis is carried out between the sample depositions. For a typical setup, the deposition time is one hour, followed by photolysis for 20 minutes. In general, this sequence is carried out four times giving a total deposition time of 4 hours and photolysis time of 80 minutes [1]. After photolysis, the window is returned to the spectroscopy position to record the absorption

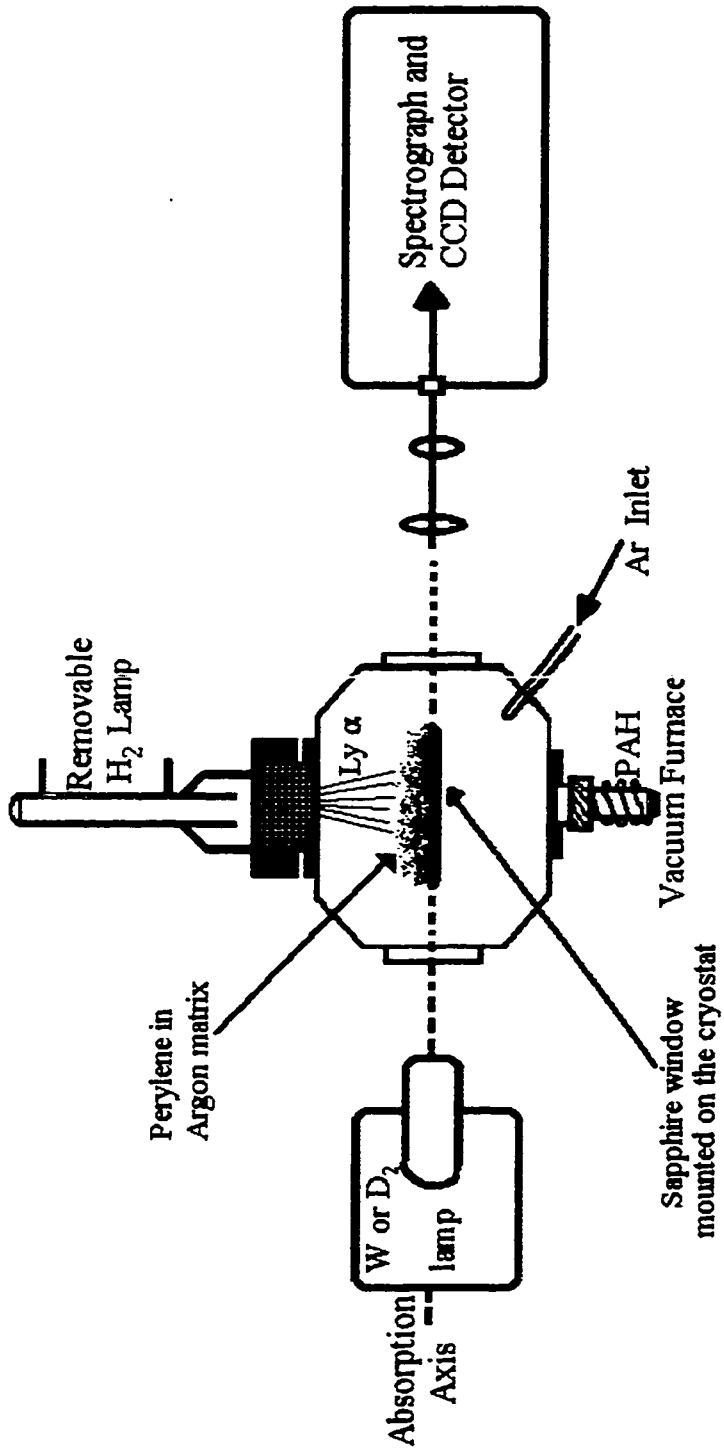


FIGURE H: Cross-sectional view of the experimental configuration for Photolysis process.

and fluorescence spectrum of the perylene cations. The outcome of the photolysis process can be observed by comparison of absorption and fluorescence spectra of neutral perylene to that of the perylene cation.

C. SPECTRAL FEATURES OF PERYLENE CATION:

I. ABSORPTION OF PERYLENE CATION :

Absorption features are very important towards the study of ionization of a particular molecule. Appearance or disappearance of any spectral features to and from the spectrum of neutral molecules is an indicative of the changes produced due to the photolysis process.

The absorption spectrum of the perylene cation isolated in a Ne matrix was taken by Joblin et. al.[32] and can be seen in Figure I. A significantly comparable spectrum of perylene in argon was analyzed by Szczepanski et. al. [29]. This spectrum can be seen in Figure J(a). In the experiments in Ref. 29, and in figure J(a) result of deposition of perylene and argon as an electron impact product are shown. For Figure J(b), the resulting sample from (a) was photolyzed.

For absorption spectrum of neutral perylene in argon matrix, no features are seen beyond 500 nm towards the longer wavelengths. The appearance of new features in the visible region is due to formation of the perylene cation. In 1990, Szczepanski et. al. applied a correlation technique by varying the energy of ionizing radiation, pressure of argon during deposition, temperature of the sample oven, matrix annealing temperature, and photolysis time. The absorption features turned out as very characteristic of the

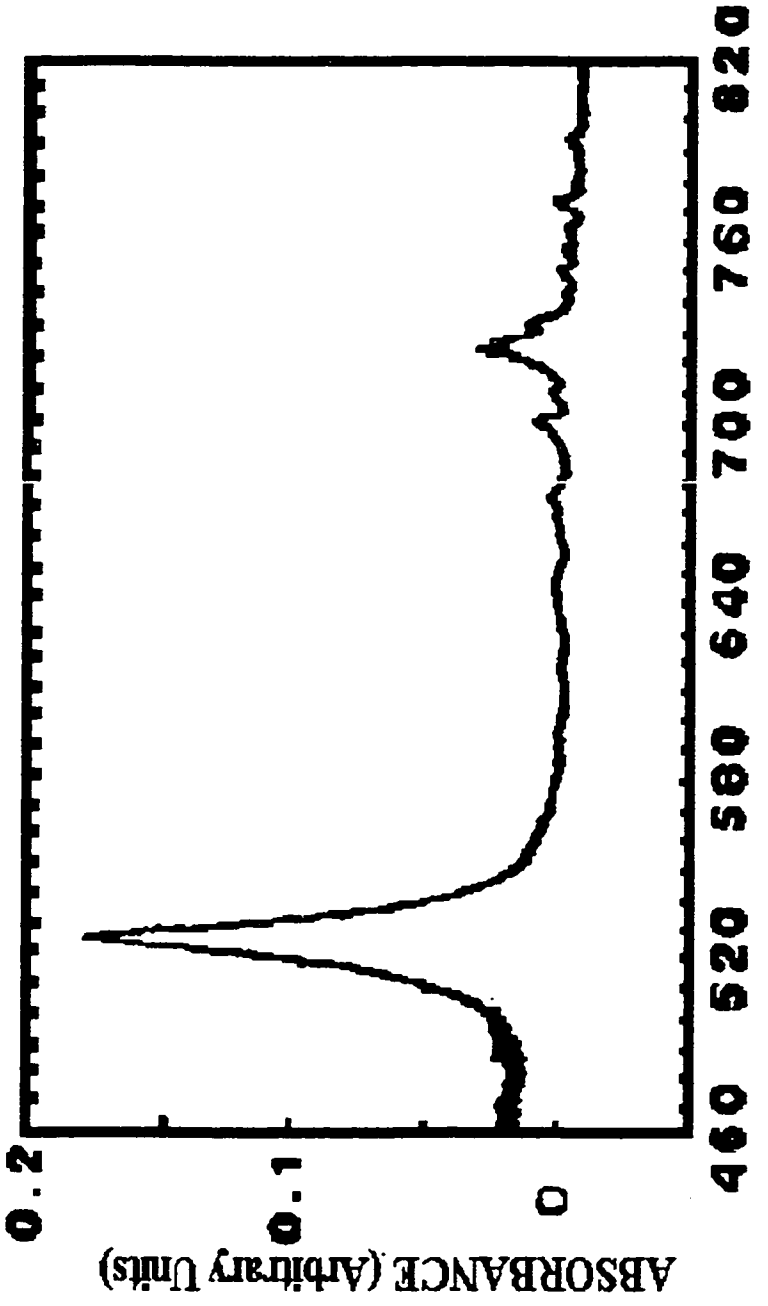


FIGURE 1: The visible absorption spectrum of perylene cation isolated in Neon matrix.[32]

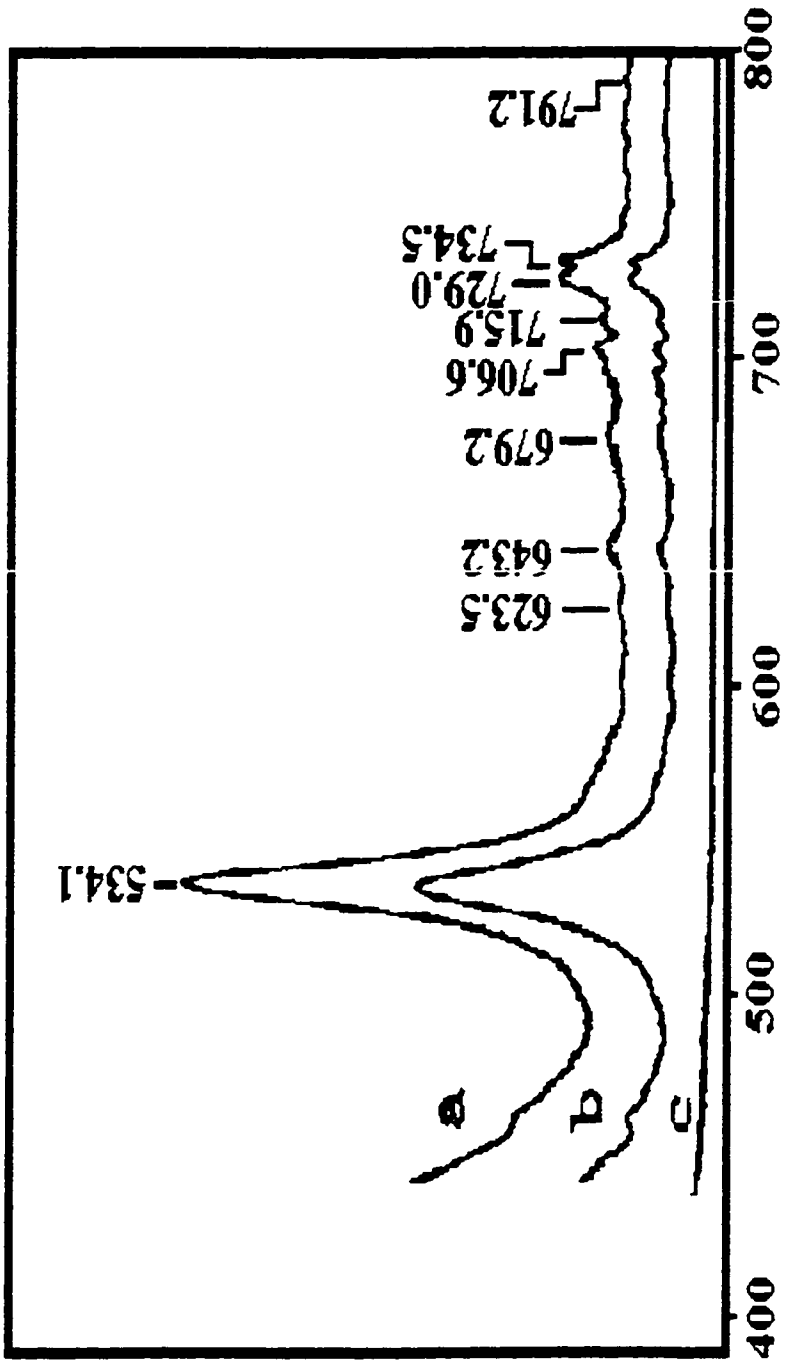


FIGURE J: (a) Absorption spectrum of perylene cation due to the deposition of electron impact products of perylene in argon. (b) Spectrum of (a) after photolysis using Hg lamp. (c) Spectrum of neutral perylene.[29]

perylene cation. Various IR features that are a result of the photolysis have also been observed that will not be discussed here.

The absorption spectrum in argon matrix and neon matrix compares very well. However, there is a shift of approximately 90 °A towards the longer wavelengths in the case of argon matrices. The strongest band observed at 534.1 nm is associated with the $D_o(^2A_u) \rightarrow D_5(^2B_{3g})$ transition [32]. The other low energy transitions are fairly weak but are clearly visible in the spectrum. The other transitions that take place in the visible region, are $D_o(^2A_u) \rightarrow D_3(^2B_{2g})$, and $D_o(^2A_u) \rightarrow D_1(^2B_{3g})$ transition [32,33].

Presence of these spectral features in the absorption spectrum indicates that there is a sufficient quantity of the perylene cations in the matrix. No additional features are seen that could be a result of the free electrons binding with some other site as they ionize off of the perylene molecules.

The structural properties of perylene in the ground and excited state are very important to consider. During the fluorescence experiments, perylene undergoes a $S_o \rightarrow S_1$ transition. It has been seen that the perylene molecule is planar in the ground and first excited states. However, there is an increase in the aromatic character in the excited state which is due to the electronic transition[34,35] that results from photolysis of the matrix.

II. FLUORESCENCE OF PERYLENE CATION:

Fluorescence spectra of perylene cation was first studied by Joblin et. al.[32] in neon and argon matrices. Emission bands were observed to the red of first absorption system.

The excitation was carried out in the region of 525.1 nm absoption band system and in the region of $D_o(^2A_u) \rightarrow D_3(^2B_{2g})$ transition, at around 723 nm. The fluorescence spectra obtained at these two different excitation regions is quite similar [Figure K]

The fluorescence feature observed at 794.1 nm was assigned to the 0-0 transition arising from $D_o(^2A_u) \leftarrow {}_1D(^2B_{3g})$ state. The basis of this assignment is that it is in the close neighborhood of 794.3 nm absorption component. Details on assignment of other emission features can be found in Reference 32.

Emission spectrum of matrix isolated perylene cation in argon matrix was also studied and compared with neon matrices, by Joblin et. al. This spectrum can be seen in figure L. The origin of $D_o \leftarrow D_1$ transition is slightly red shifted as compared to that of this transition in absorption. All strong bands were assigned to perylene cation based on the excitation spectroscopy.

Recently, Chiller et. al.[36] studied the fluorescence of perylene cation in an argon matrix on excitation in the ultraviolet spectral region. The region around 248 nm is the strongest absorption region of neutral molecule. Ionized perylene shows a transition in that region which is indicative of perylene molecule not undergoing significant structural changes as it is ionized[33].

In the laser-induced fluorescence spectrum obtained by Chillier et. al [36], transitions of the perylene cation was red shifted as compared to the neutral molecule. This red shift was attributed to the destabilization of the electron ground state due to photolysis of the molecule. The ground electronic state of the ion was assigned as lying

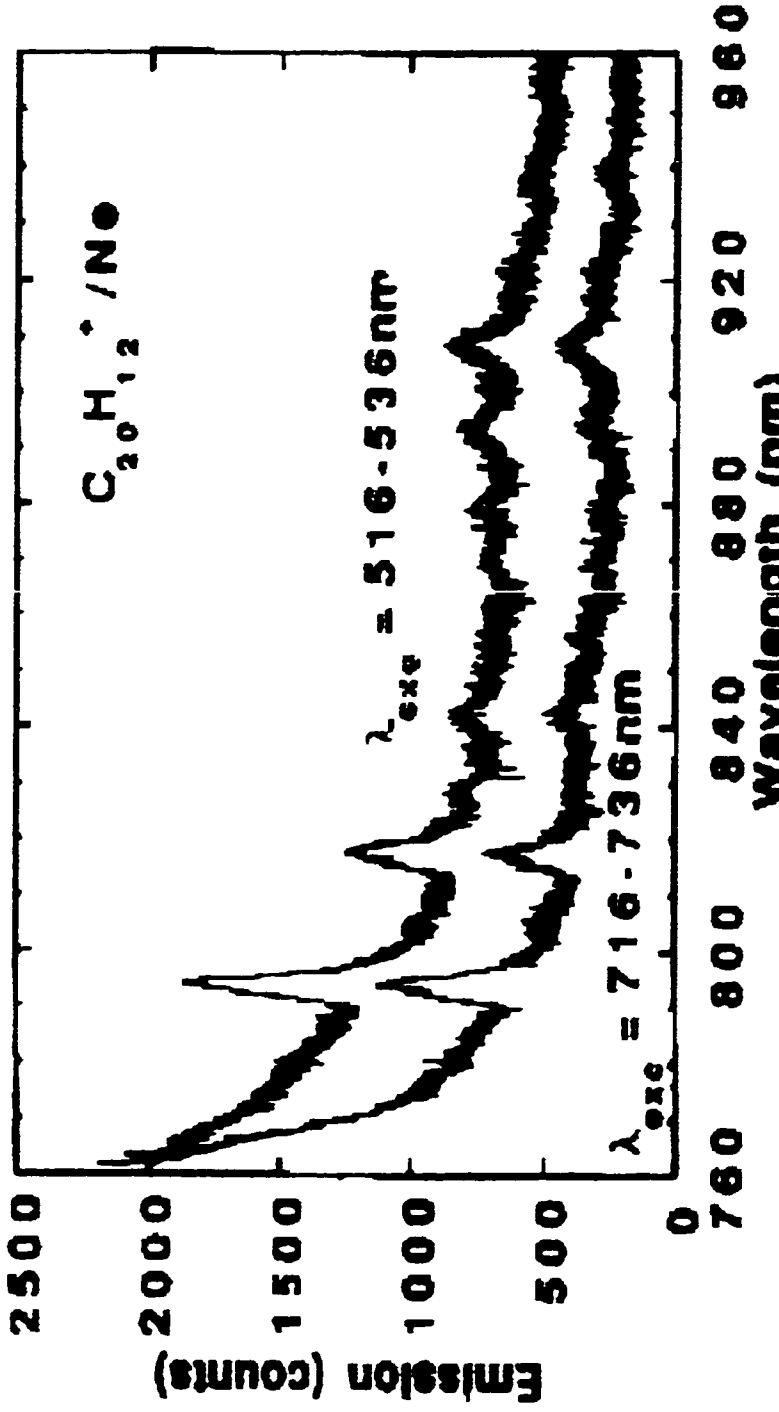


FIGURE K : Fluorescence spectrum of matrix-isolated perylene cation induced by pumping absorption bands at 525 nm and near 723 nm.[32]

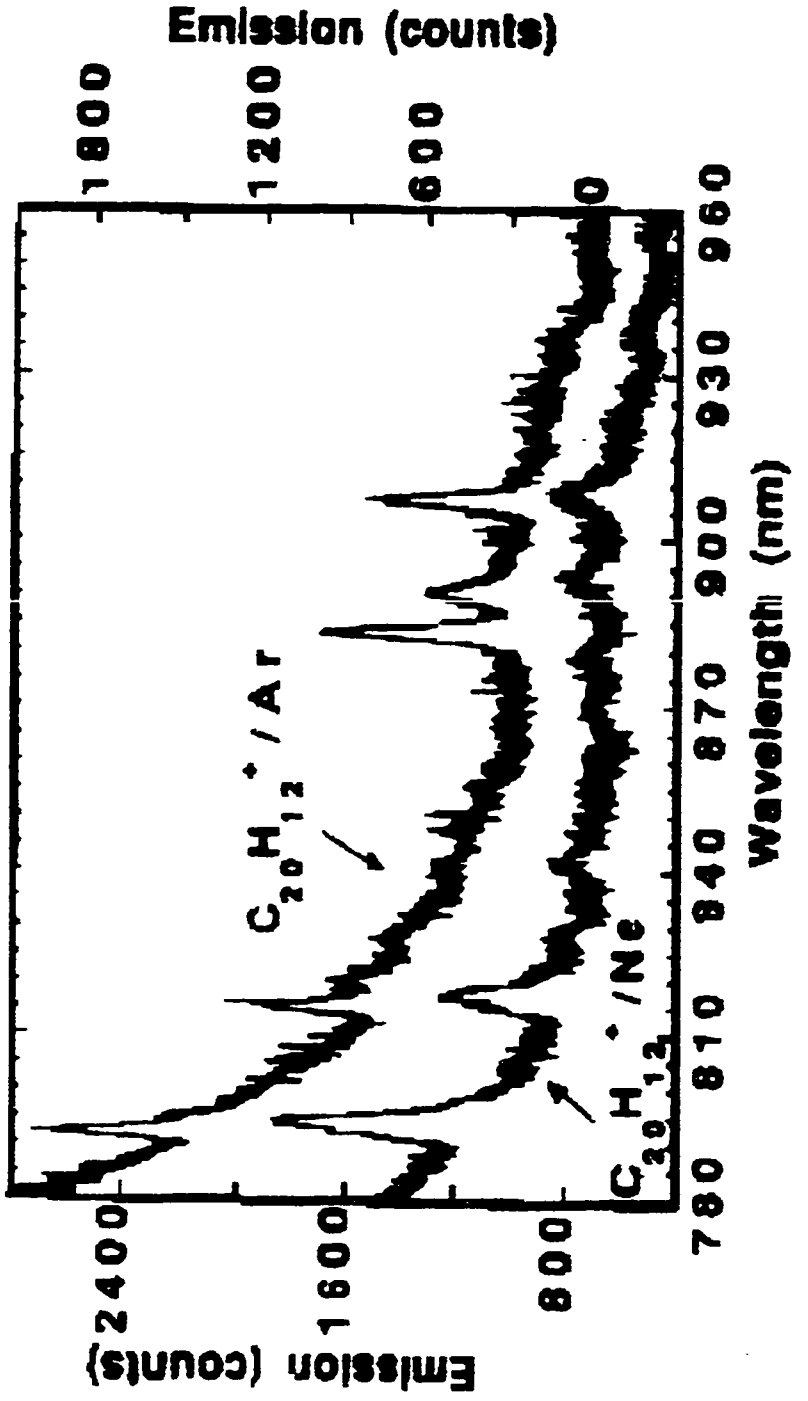


FIGURE L : Fluorescence spectrum of perylene in argon and neon matrices.[32]

at a higher energy than its neutral homologue. This fact also leads to the suggestion that perylene may be considered to be made up of two naphthalene nuclei [37].

III. RECOMBINATION PROCESS IN PERYLENE:

One of the advantages of matrix isolation spectroscopy is that the same matrix can be used to perform several sets of experiments. Once the absorption and fluorescene experiments are completed, the matrix provides useful information as it is being destroyed.

In matrix-isolated perylene, as the matrix is warmed up, a flash of light is observed which may be due to the electron-ion recombination process in perylene. Detailed discussion on this behavior of perylene can be found in Appendix C.

IV. THERMALLY STIMULATED LUMINESCENCE IN PERYLENE:

The electron-ion recombination spectrum of perylene can be seen in Figure M. Figure N presents a higher resolution spectrum for the same process. This spectrum appears to be made up of the spectral features of neutral perylene and a progression that begins at 398 nm and goes up to 640 nm. Contrary to a normal progression, the spectral lines in this spectrum have a larger difference between them as we move towards the longer wavelengths.

As we compare the fluorescence spectrum of neutral perylene to the recombination spectrum, we see that some of the neutral bands can still be observed. The bands at 434, 440, 460, 463, 490, and 496 nm can be assigned to the neutral perylene. This leaves the features that are a part of the progression only. The separation

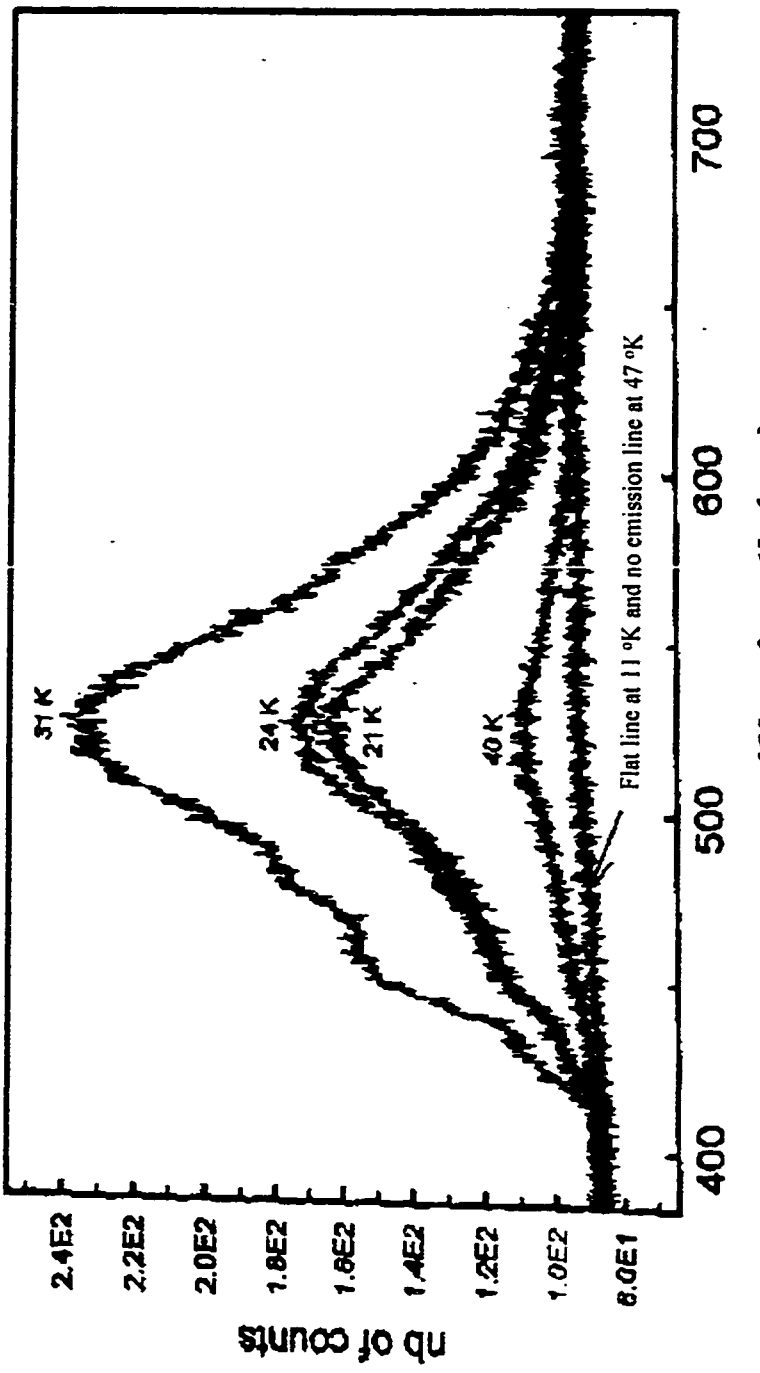


FIGURE M : Low resolution spectum of recombination process in Perylene.[1]

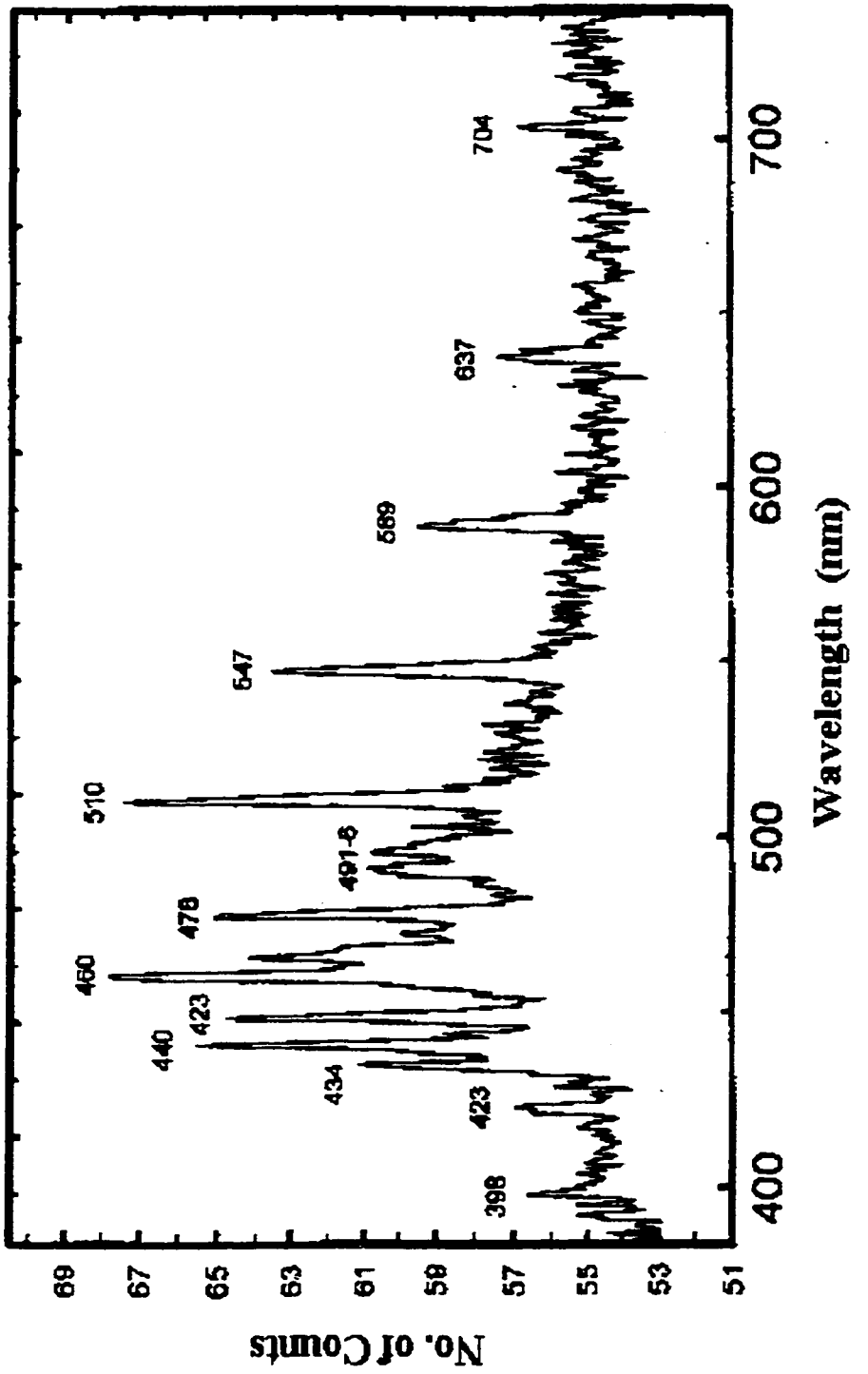


FIGURE N: Luminescence of Perylene cation due to Electron-Ion recombination[1]

of these features increases from 24 nm to 40 nm as we move towards the longer wavelengths.

The remaining features of this spectrum possess a pattern that resembles that of diatomic type molecules, differing only in the spacing increases as we move towards the red. This is opposite to what one would expect from the spectrum of a diatomic molecule. However, no matches of these features were found to resemble any diatomic molecule.

Moreover, some of these features were found in the fluorescence spectrum of perylene in solution. The 547, 510, and 478 nm features were reported by Shpol'skii and Personov in 1960 [20]. None of these features appear in the matrix isolated fluorescence spectrum or in the ethyl alcohol solution. No spectral features beyond 551 nm were reported by Shpol'skii. The shorter wavelength features could not be compared as the fluorescence spectrum is slightly red shifted as compared to the recombination as well as the fluorescence spectra using matrix-isolation. The 398, 422, and 448 nm features lie in the absorption region of the matrix isolated perylene. These features can be seen in Figure E. Hence it may be assumed that there is some absorption phenomenon occurring along with the recombination process of electrons and cations that is attributed to the characteristics of perylene itself.

An experiment was performed by Chillier et. al. to examine the behavior of matrix deposited argon with no added amounts of perylene. A spectrum was obtained that can be seen in figure O. This spectrum shows a long progression that appears to be a part of the TSL spectrum of matrix deposited perylene. However, when this experiment

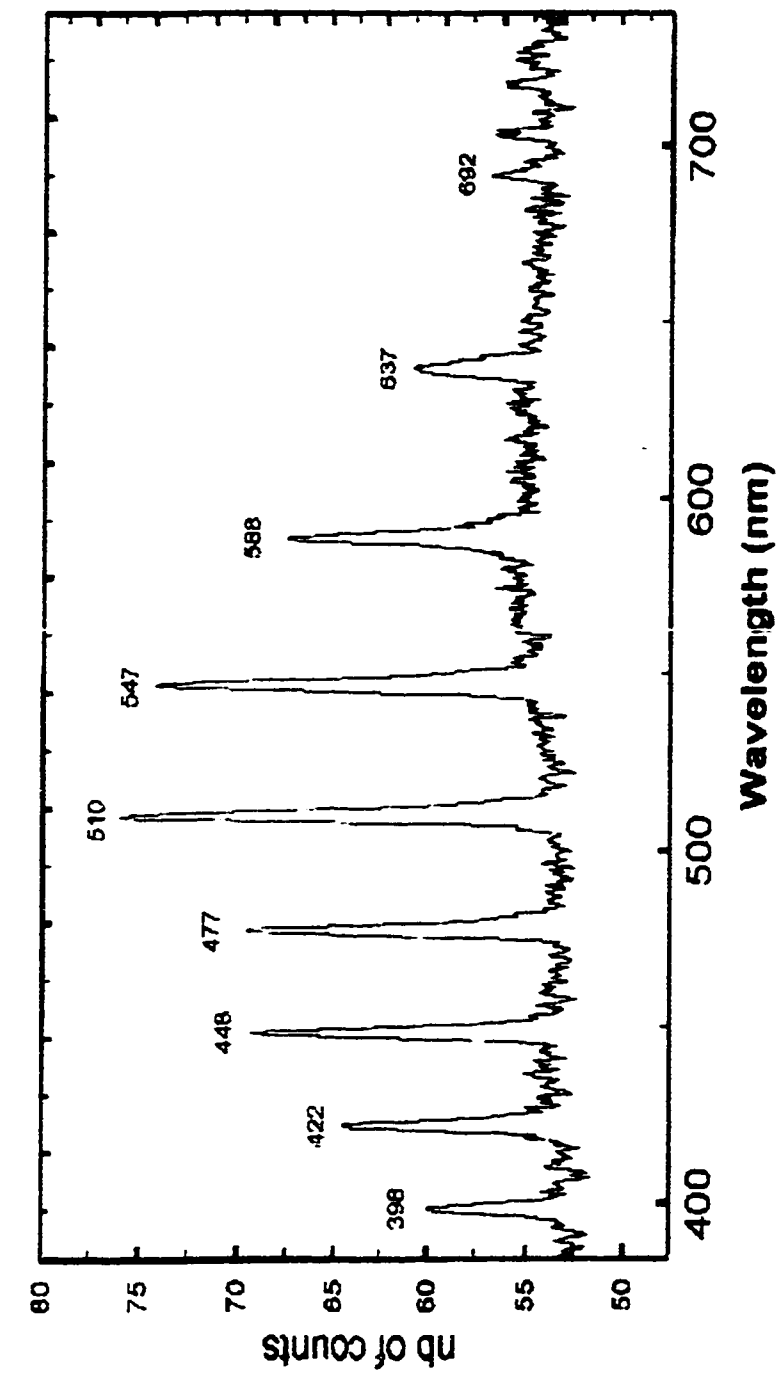


FIGURE O: Thermally stimulated luminescence for a matrix without any deposited perylene

was repeated to check reproducibility, no emission was seen at all. Therefore, this feature may be attributed to some contamination in the system that could have been left over from the previous experiments on perylene.

To observe the match to these features from figure O, fluorescence spectrum of perylene cation was subtracted from TSL spectrum. The subtracted spectrum can be seen in figure P. This spectrum presents features that are comparable to those seen in Figure O. As these features were not reproducible as in figure [O], these can be characteristic of perylene molecule itself.

The electron-ion recombination spectra of perylene were also carried out by gradually increasing the temperature of the matrix. For matrices with Perylene/Ar concentration of approximately 1:1000, the recombination spectra with a gradual temperature increase can be seen in Figure Q. The recombination bands are visible up until approximately 38 °K. Beyond this temperature, the matrix is destroyed and no features are visible.

Interestingly, the recombination rate is very dependent upon the concentration of perylene molecules in the matrix. For a typical matrix of Perylene/Ar, with a ratio of approximately 100:1000, the recombination process is complete at around 30 °K. The series of the spectra can be seen in Figure R. However, this spectra had various interferring spiking bands that are due to the electrical spikes and are not representative of the matrix itself. The spectra in Figure R has been modified by removal of those spiking bands and can be seen in Figure S.

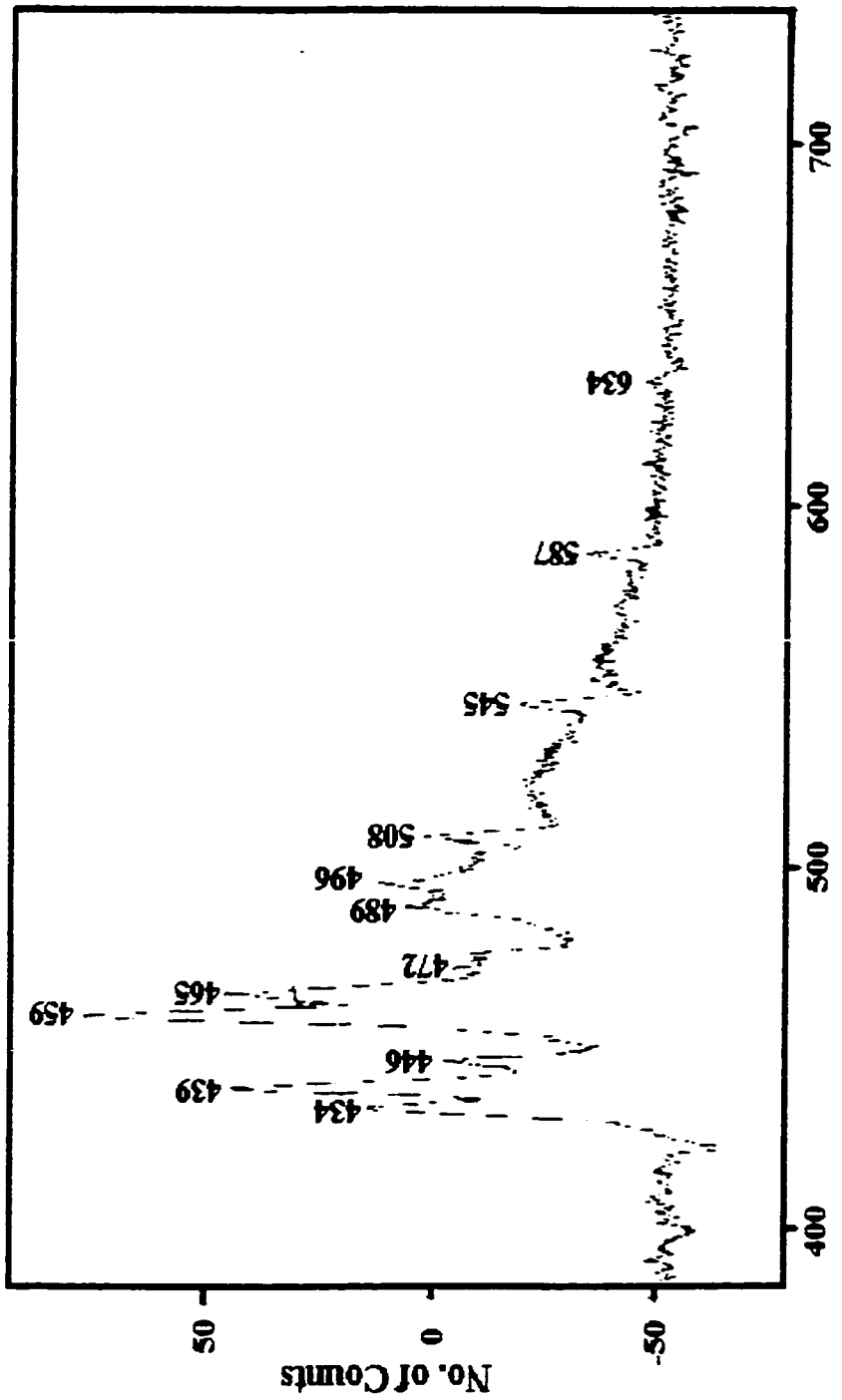


FIGURE P: Spectrum from Figure [O] subtracted from Figure [N]

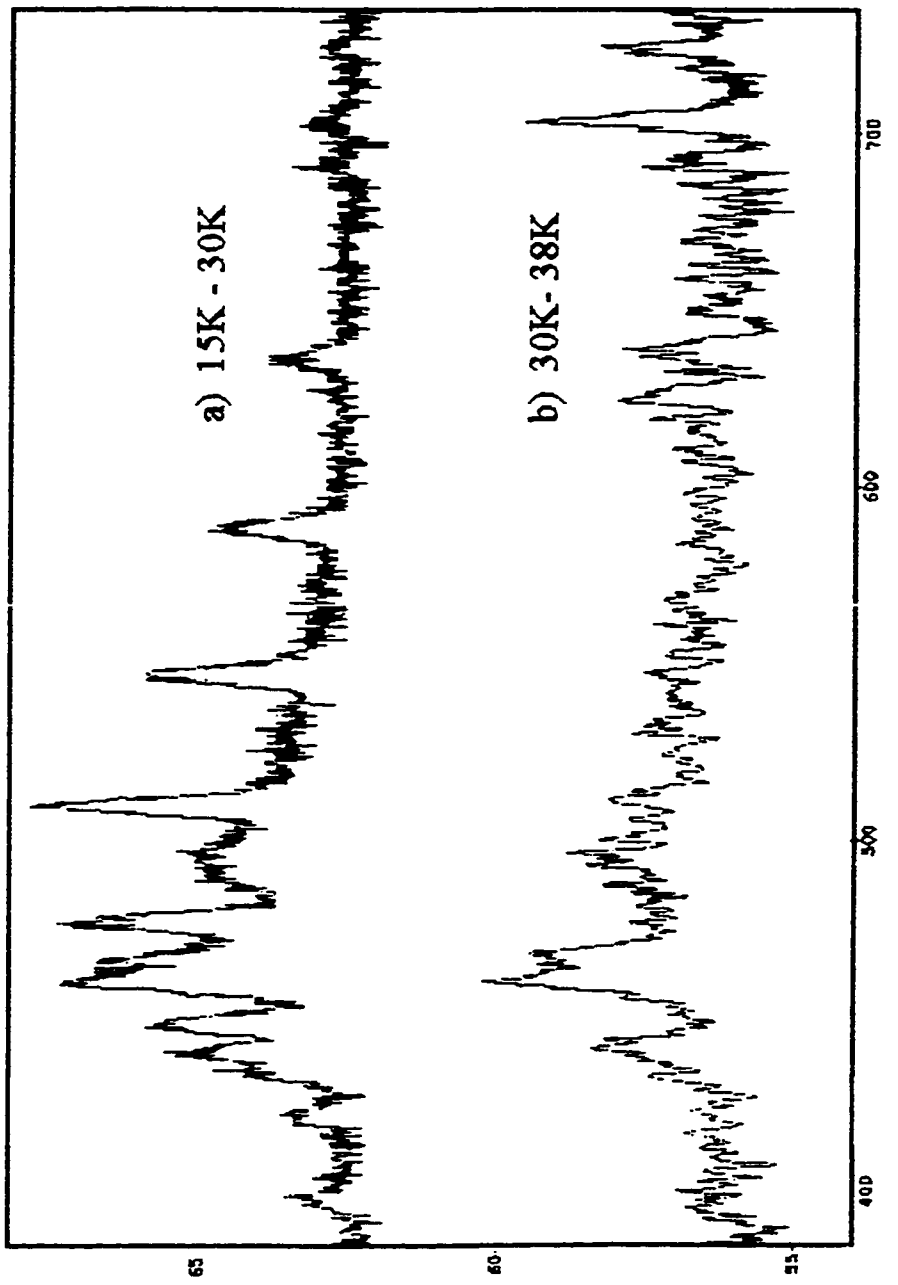


FIGURE Q: Recombination spectra of Perylene cation with less abundance of Perylene molecules.[1]

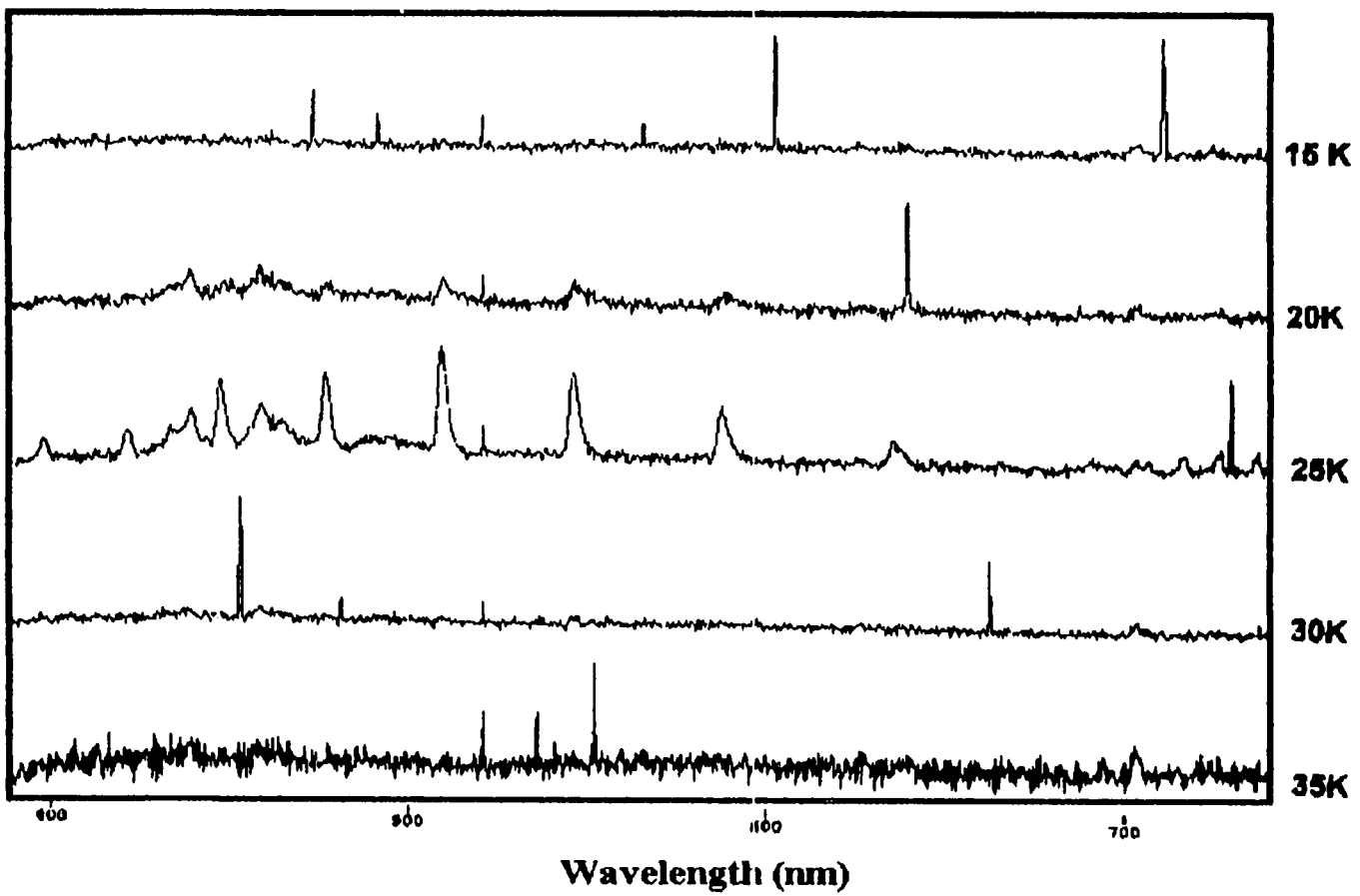


Figure R: Recombination Spectra for Perylene ion in Argon matrix at different temperatures.

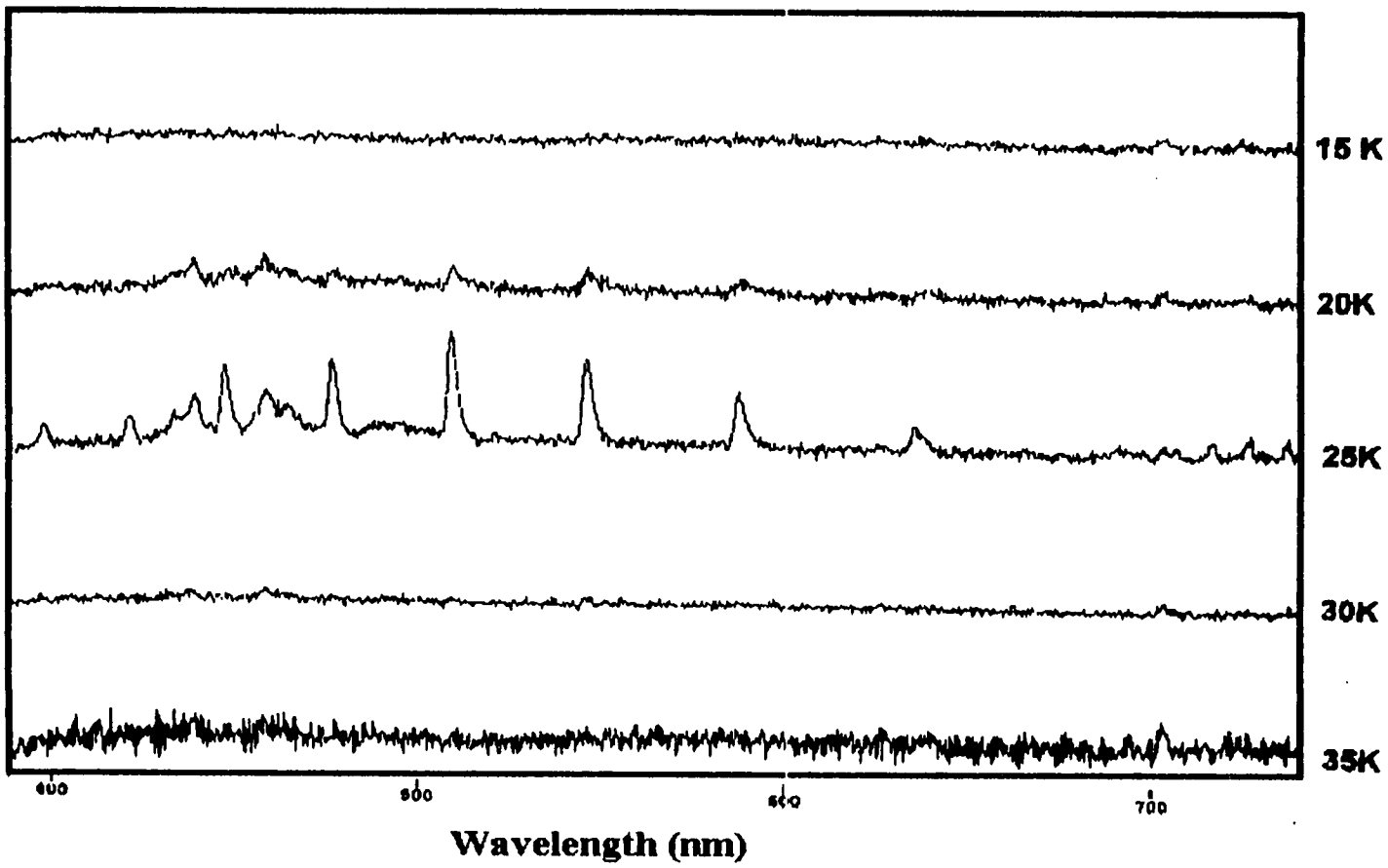


FIGURE S: Modified recombination spectra of Perylene by the removal of interfering spiking bands

This temperature dependence of recombination process can be explained based on the mobility of electrons. In the matrices with lower concentration of perylene, electrons have to travel more distance to find a perylene cation to bind to. Whereas, in matrices where the perylene abundance is fairly large, it is easy for electrons to find the cations. Hence the recombination process can take place in a shorter time and at lower temperatures as compared to the matrices where the perylene concentration is fairly less.

The ionization and hence recombination was tried based on different concentrations of perylene in the matrix. It was seen that no ionization was possible if the perylene concentration was too high, i.e. the formation of perylene clusters. In that case, as soon as the electron comes off one perylene molecule, it immediately combines with another perylene cation as the distance between the perylene cations is significantly less. The absorption spectra of perylene clusters resembles that of the perylene crystals, with a strong broad band at room temperatures that gives fine structures that is shifted towards the shorter wavelength at lower temperatures [38].

Astrophysically, the recombination reactions have been studied in case of plasmas at significantly high temperatures. In the regions of low temperatures, recombination reactions may also be possible as shown by the matrix isolation studies.

Considering the amounts of dust present in the interstellar medium, it is more important to picture it as having minimal amounts of the organic species. The starlight serves as the excitation source. As the electrons would randomly revolve seeking some binding site, they may possibly return to some cationic species of polycyclic aromatic hydrocarbons, if present, to undergo the recombination process.

CHAPTER VI. FUTURE STUDIES:

Thermally Stimulated Emission in PAHs is a term that has been recently studied at the Astrochemistry Lab of NASA Ames Research Center. Perylene has been the only molecule studied for TSL so far.

Future research in this field would involve performing these experiments on other PAHs. Other homologues of perylene series are terrylene, and quarterrylene. These molecules have the possibility of showing recombination features similar as those of perylene. Derivatives of perylene such as Benzo(ghi)perylene and benzo(e)perylene are other possible candidates.

The recombination spectrum of perylene shows a progression that appears to be a result of emission from one excited state to the different lower vibrational levels of ground state. This feature needs to be studied in detail and experiments need to be performed on different PAH molecules to observe any similarity between these recombination features.

Naphthalene would be another molecule of particular interest. Results of this may relate to the luminescence shown by perylene, as perylene is considered to be made from two naphthalene nuclei, that are joined by weak single bonds.

APPENDIX A

MATRIX ISOLATION -TECHNIQUE

The matrix isolation technique and experimental conditions described here are those used by Chillier et. al.[1]. This experimental set-up is also similar to that in Ref. 39 and Ref. 40.

The experimental apparatus is comprised of an ultra-high vacuum system that consists of a cryogenic sample chamber. This sample chamber has four ports at 90° to one another. These ports are inclined in such a way that two of the four ports face one another. There are two gas injection ports at 45° to one another. The substrate is a sapphire window mounted on a cryostat. The sapphire window is held inside the stainless-steel high-vacuum chamber in such a manner that it can be rotated through 360° without breaking vacuum. This window can be positioned to face the spectroscopy window, gas injection port, an excitation source, or vacuum deposition furnace depending upon the experimental requirements. The window is suspended at the center of vacuum chamber and is cooled down to 10 K by a variable temperature, continuous flow- liquid helium cryostat. The temperatures are monitored by a thermocouple attached to the cryostat.

The typical spectral light source for ultraviolet and visible spectroscopy is a 160-360 nm output Deuterium lamp. The computer-driven monochromator is equipped with three interchangeable gratings of variable linear dispersion blazed at 300 & 650 nm for ultraviolet and visible-near infrared spectroscopy respectively. The entrance slit of

spectrograph is typically at 60-70 μm for absorption experiments, and 100-150 mm for emission.

The photon detector is a thermoelectrically cooled, charged coupled device (CCD) area array detector that is sensitive in 180-1060 nm range. The CCD is mounted directly to the exit port of monochromator and is interfaced to the computer system.

The typical ionization source is a microwave powered, flow discharged hydrogen lamp generating photons of 10.2 eV energy (Lyman α line, $\lambda = 120$ nm).

The initial process of preparing sample matrix is co-deposition of the PAH sample and argon gas onto the cold (10 K) substrate. The sapphire window is held in such a way that it is slantingly facing the gas injection port, and the vacuum system that holds sample. Small amounts of PAH samples are placed in a Pyrex tube that is attached to the vacuum system in such a way that it is at 90° to the gas injection port. The tube is wrapped with heat tape and can be warmed to a particular temperature at which the PAH begins to sublime. As the sample is heated, argon gas is also introduced through the adjacent port in such a way that it can be directed towards the window along with a large quantities of argon. This schematic of the experimental setup can be seen in Figure T

The two beams of the PAH and argon, coalesce at the surface of window and freeze. As a result, each PAH molecule is isolated from one another and undergoes minimal interactions. The interactions of PAH molecules with argon matrix are extremely weak due to the inert nature of argon. The molecule under study is, therefore,

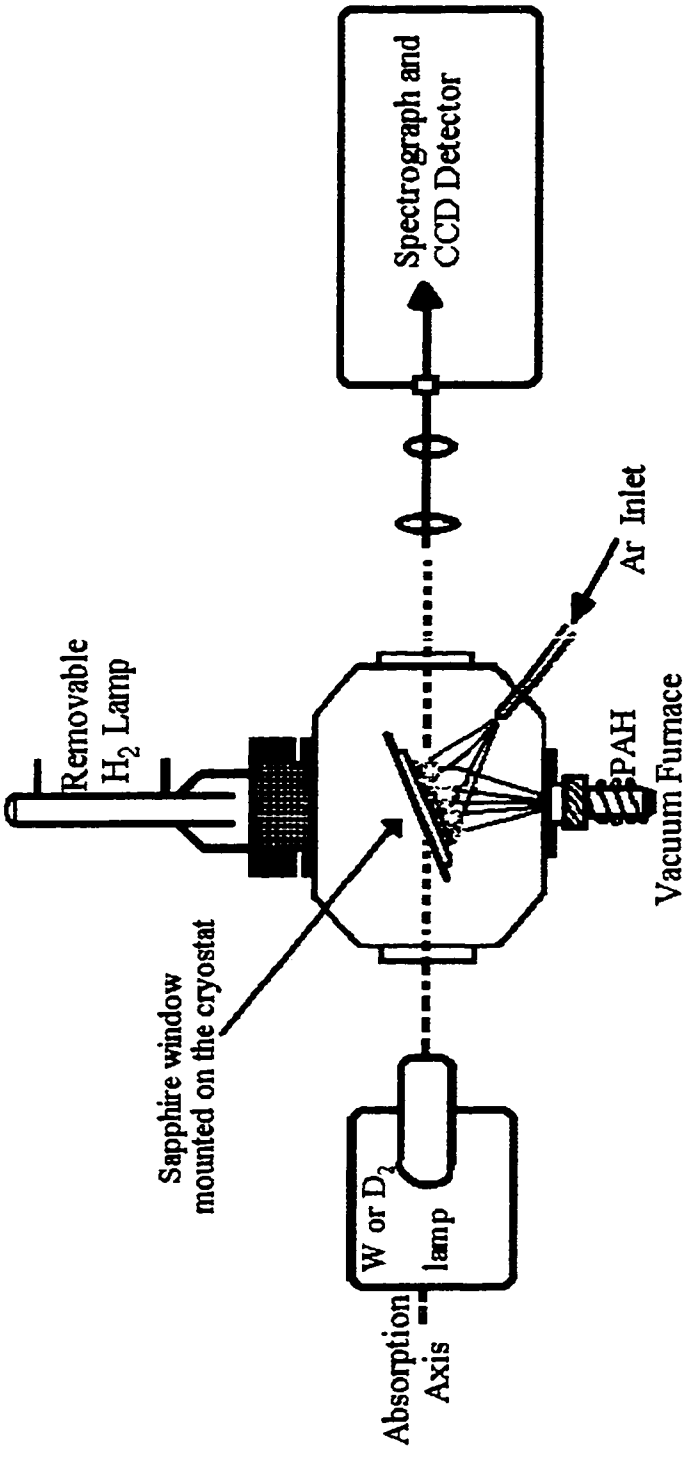


FIGURE T: Cross-sectional view of the experimental configuration for sample co-deposition.

'bottled up' in a pseudo-isolated state, and this condition can be maintained for as long as the matrix is maintained.

The sample deposition process is usually carried out for one hour. The process is paused for some time to photoionize the deposited sample. In order to do the ionization, sapphire window is rotated to face the excitation source i.e. Hydrogen Lamp. The setup is as shown in Figure H. The sample is photolyzed for 20 minutes at that configuration. Once the stable precursor has been set to the vacuum UV photoionization, the sample is returned to the spectroscopy position. The process of deposition is started again by continually keeping the substrate at 10 °K. The process of deposition is repeated a couple of times as required for the experimental procedure, and is always followed by photoionization. The time for deposition and photolysis are varied depending upon the molecules under study.

Once the desired quantities of sample and inert gas are deposited on the sample window, the matrix is ready to perform absorption, fluorescence, and finally the electron-ion recombination process.

Before the recombination experiment, the system setup needs to be completely isolated from all outside light sources. In other words, the experiment is carried out in totally dark conditions. A background spectrum is obtained before beginning of the experiment. The cooling system is then turned off, or set to a specific temperature, depending upon the requirements of the experiment. The temperature of the window slowly starts increasing. The electrons that were driven off of the PAH molecule due to

photoionization, now tend to come back to the ionized species, giving off energy in the form of light causing the thermally stimulated emission. This process is visible as a faint flash of light.

APPENDIX B

TRAPPING AND RELEASE OF ELECTRONS IN MATRIX-ISOLATED PERYLENE

The photolysis of perylene in an inert gas matrix produces a significant count of electrons that are deprived from the parent molecule. Electrons that are freed from the parent molecule have a tendency to search for a binding site that they can attach to in the matrix and stabilize. One of the necessary conditions to perform electron-ion recombination experiment is to hold these electrons in a free or loosely bound state inside the matrix system. However, this binding site is not the parent molecule itself. In other words, electrons do not come out of one perylene molecule and bind to another. This is explained by the formation of ionic bands in the absorption spectrum of photolyzed perylene in argon matrix [Figure I].

The matrix isolated system can be considered as a molecular solid of inert gas atoms with PAH molecules as impurities intact with the nearby atoms. As this matrix is photolyzed, electrons come off of the PAH molecules and search for an impurity or some other electron scavenger with which they can bind.

The electrons carry significant amount of electronic charge. Once removed from the parent atom, as they come in contact with excess of inert gas atoms, the inert gas atoms experience an additional coulombic force which alters their equilibrium position in the matrix [Figure U]. These atomic displacements are such as to lower the potential energy of the electron. If the potential well produced by the atomic displacement pattern is sufficiently deep, the electron may occupy a bound state. In this case, the electrons

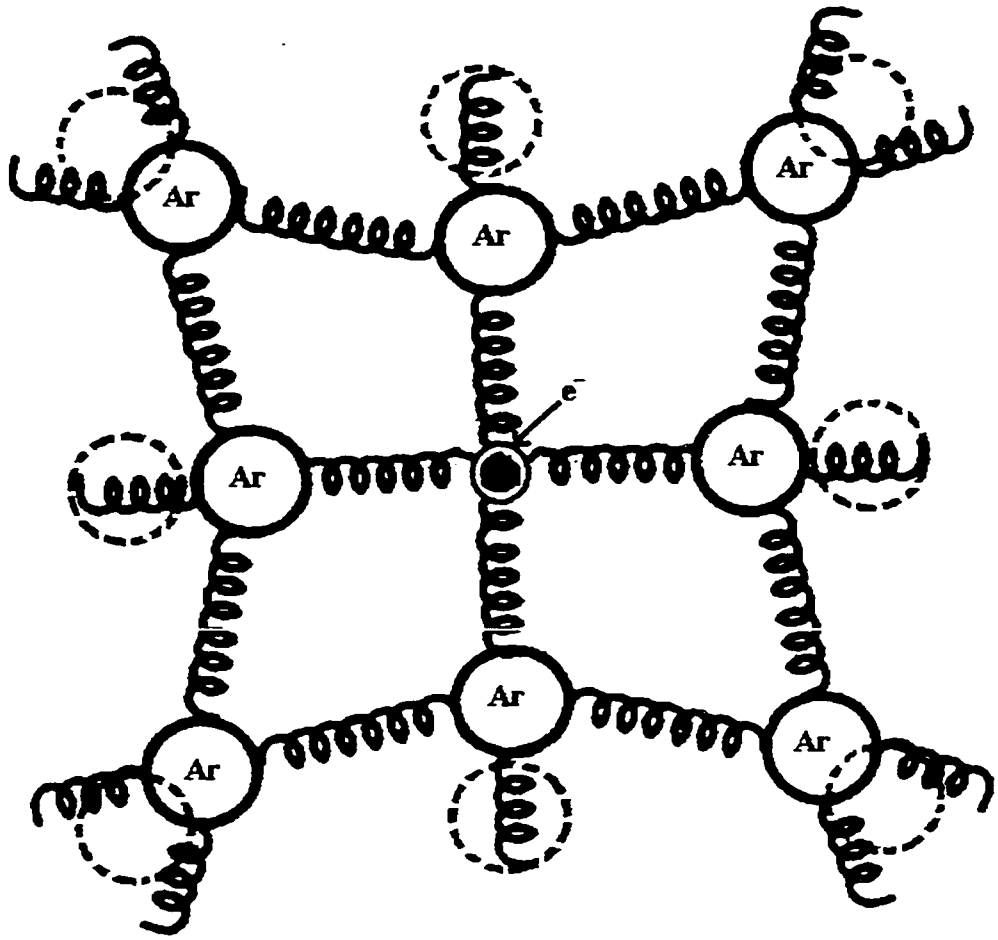


FIGURE U: Displacement of neighboring atoms by the free electron. The electron here is represented in the center of the Polaron unit. The dotted circles represent the original positions of the Argon atoms.

cannot escape from its position in the matrix without a change in the position of surrounding atoms. The change in position, in this case, is due to the change in mobility as the temperature is increased. The potential well that binds the electron, is a result of atomic displacements caused by the presence of excessive coulombic charge. Therefore, the electron is said to be 'self trapped' [41]. In other words, the electrons are held within a pattern containing the surrounding atoms, and therefore are self-trapped into their own potential well [Figure V]. These severely localized electrons within a potential well, are known as *Small Polaron* [42]. The term 'polaron' refers to the entire unit comprising the self trapped electron and the atomic displacement pattern.

The frequency dependence and the Hall effect for small polarons significantly differs from the similarly charged free particles. Interactions between small polarons differ significantly from those of free particles.

The term 'small' is used when the spatial extent of wave-function of the excess electron is less than or comparable to the separation of the atoms or molecules. In other words, the characteristic radius of the electron is much less than the interatomic separations between the argon atoms. The electrons then move only in response to the motion of surrounding atoms. A small polaron has mobility less than 1 cm^2/V sec and it increases with increase in temperature.

The interactions between small polarons may be significantly different from those of simple stationary charges. The reason for difference is that in addition to the direct Coulombic interaction of the charges, small polarons interact via the overlapping of the atomic displacement patterns. In the case of the matrix-isolated spectroscopy, the

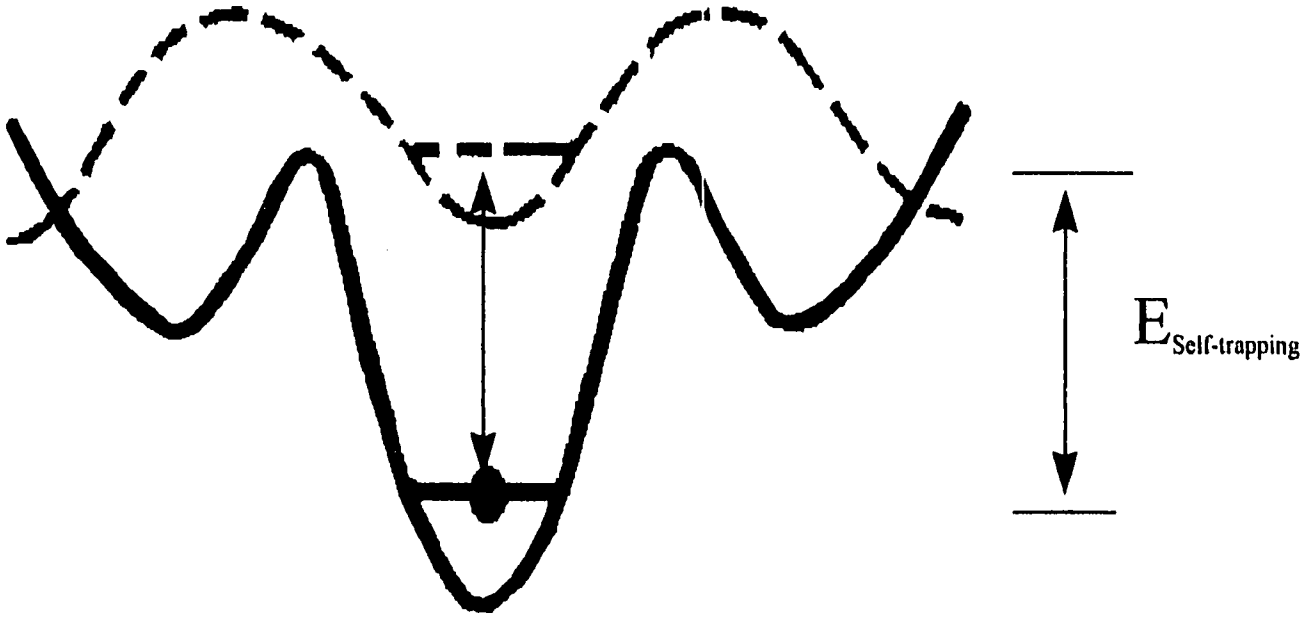


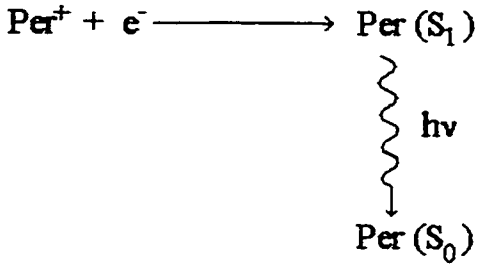
FIGURE V : Potential energy curves for the undisplaced atoms in a matrix (dotted curve) and for the displaced atoms (solid curve).

amounts PAH molecules are significantly less than those of argon. The electrons are most likely to form a deformed pattern involving mainly the argon atoms. Due to the inert nature of the argon atoms, there are negligible interactions between the deformed patterns involving the self-trapped electron.

Under these conditions, a significant amount of energy is needed for the interactions between atoms to come into being. The self-trapped electrons, or small polarons, have less energy than an electron in a perfectly rigid solid. The energy of the polaron is lowered by its binding energy E_b which is the difference between the self trapping energy between the potential wells of undisplaced and displaced atoms, and the strain energy associated with deformation of the lattice. The motion of an electron in a self-trapped state is restricted to the potential well of its own creation. The movement of electrons held in a deformed lattice not only needs transfer of electron, but the polaronic unit as well. The latter involves quantum mechanic tunneling of the atoms comprising the displacement pattern. [figure U]. The polarons would be able to interact with another unit only if there is sufficient energy for the entire unit to undergo tunneling.

This energy for the polarons to destruct into stationary free charges, i.e., free electrons, is provided by the warm up of the matrix. As the matrix is warmed, the self-trapped electrons gain mobility and hence sufficient energy to escape out of their potential well. These electrons once again, search for some site that they can bind to. Within the matrix, there are perylene molecules that are now in the form of perylene cations. The free electrons have a tendency to readily bind to the perylene cations. As the electrons bind to the perylene cation, perylene turns into an excited neutral molecule

state. This then relaxes non-radiatively into the neutral perylene molecule. The recombination process involves the following:



This transition is a ($\pi\pi^*$) transition [43]. This process is possible when the electrons are no longer a part of the polaronic unit. The energy the electron gains through the warm-up process is sufficient to tunnel and then to destroy the small polaron unit

APPENDIX C
THERMALLY STIMULATED EMISSION:

Thermally Stimulated Luminescence (TSL) is a physical phenomenon that involves emission of light during warm-up of a solid sample with the precondition that the sample is subjected to a natural or artificial irradiation. The artificial irradiation for the electron-ion recombination processes in a rare-gas matrix is provided by the photolysis process that ionizes the PAH molecules under observation.

When an electron is ejected from its parent molecule by a photon or by collision with a charged particle, if it is not removed too far away, it may recombine with its parent ion. The possibility of such electron-ion recombination was pointed out long ago by Rutherford. As an electron is ejected from its parent molecule, it produces a positive charge or a hole. The ejected electrons may be held by some other species in the sample or by weak Van der Waal interactions [44]. This electron capturing state is referred to as *trap*. Similarly, the holes may be preserved for some time. The hole capturing state is called *luminescence center* or *recombination center* [45].

TSL is a result of the high energy electrons trapped within the specimen. Heat frees the electrons which produces light much like fluorescence. One necessary condition to observe TSL is the isolation of system from any other outside light source. In other words, the experiment must be carried out at 'dark room' conditions. Presence of other light source may stimulate the matrix and the observed spectra will not just be the characteristics of the molecules of interest in the matrix. The experimental setup for TSL process can be seen in figure W.

This type of luminescence only occurs if the heating was preceded by an irradiation due to ionizing radiation. This in case of the matrix-isolation, Lyman α line from the Hydrogen lamp is used to photolyze PAH molecules.

One of the points that remains unclear in TSL is that the heating is *not* the main source of emitted light. The initial excitation is the main source of energy [46]. Warm-up of the matrix serves only as a trigger to help the release of this accumulated energy. Thermally Stimulated Emission or TSL is thereby, a more descriptive term than Thermoluminescence (TL), which is a traditionally used term.

For the matrix isolated species, trapping of electrons is attained by formation of small polarons. The electrons are held in the potential well that is created by the displacement of neighboring atoms due to weak interatomic interactions. The placement of the electron amidst the argon atoms, and the polaron unit acts as a trap for the electrons. In order for this electron to rejoin with the parent atom, it first needs to overcome the energy barrier created by lowered energy of polaron. A polaron always has lower energy as compared to the electron as a free particle.

The warm up of matrix, which acts as a trigger to the TSL, first frees up an electron from its self-trapped state. Once that electron is freed up from the interatomic interaction pattern of the rare gas atoms, that is the destruction of small polaron unit, it searches for some source for stabilization. As the area within the sample chamber is fairly small, it is easy for the electrons to locate the positively charged perylene ions. The electrons then occupy positions at the recombination centers of the perylene molecule and stabilize by transferring the excessive charge. However, this

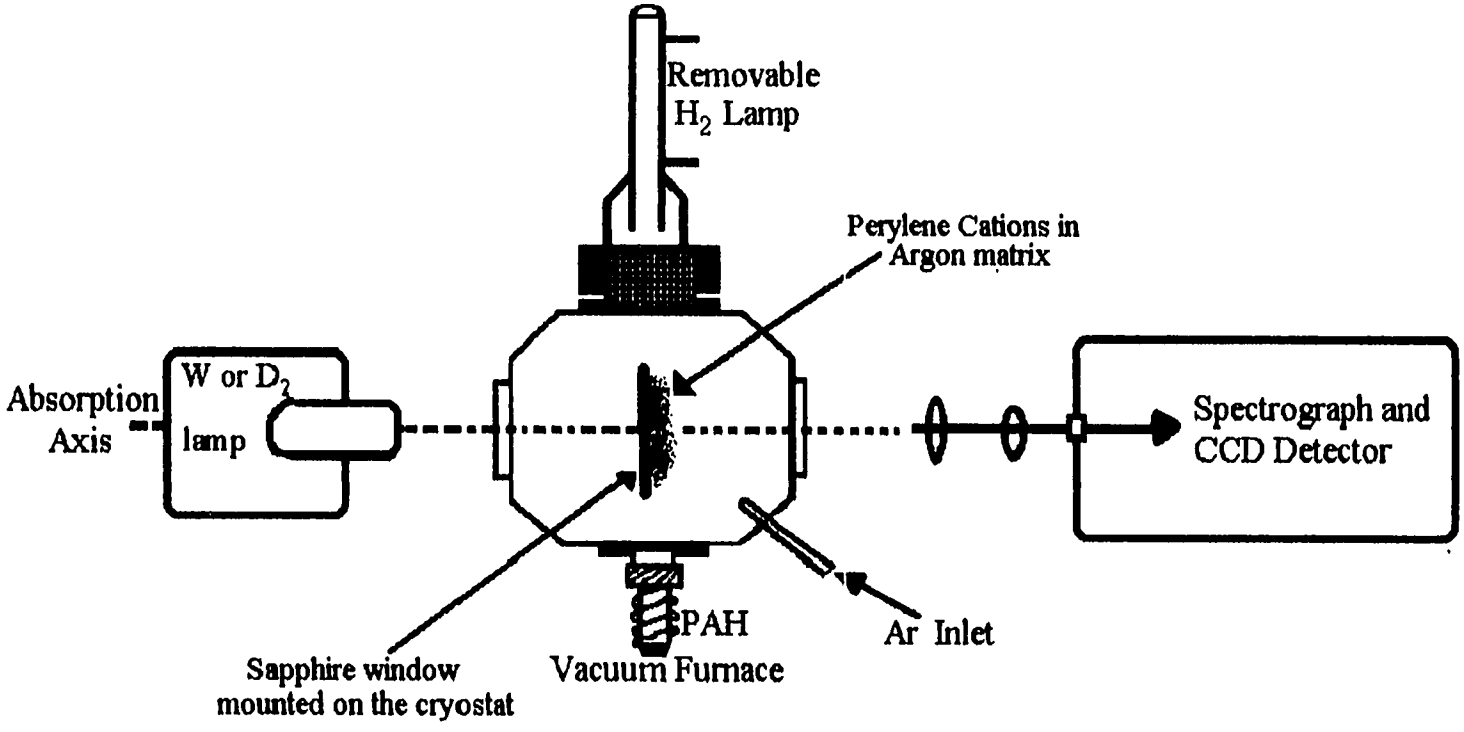


FIGURE W: Cross-sectional view of the experimental configuration for Thermally Stimulated Emission

recombination rate would depend upon the abundance of perylene ions. If the number of ions were small, the process would take longer to undergo the recombination. Whereas in significant amounts of ions, less electrons mobility is needed for electrons to locate an ion and recombine with it. This effect can be seen with gradual temperature increases when the amounts of perylene in the matrix are varied. Figure {Q} is a spectrum of perylene TSL when quantities of perylene in argon are at the order of 1/1000. For Figure R spectrum, perylene and argon are at an approximate ratio of 10/200.

CHAPTER VII.

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